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Slow dynamics of aluminium-citrate complexes studied by ^{1}H- and ^{13}C-NMR spectroscopy

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Contents

Abstract

Inter- and intra-molecular exchange reactions of the major Al(III)-citrate (Cit) complexes have been studied under equilibrium conditions in aqueous solution by ^{1}H- and ^{13}C-NMR using band shape analysis and magnetization transfer methods. Rate equations and activation parameters have been evaluated from concentration, pH and temperature dependent studies. The lability with respect to ligand exchange was: $Al(Cit)_2^{3-}$ ($k_{298} = 1.1 \pm 0.1$ s^{-1}) > $Al_3(H_{-1}Cit)_3(OH)_4^{7-}$ (*Sy*; $k_{298} = 0.08 \pm 0.01$ s^{-1}) ≫ $Al_3(H_{-1}Cit)_3(OH)^{4-}$ (*As*). The variation in lability appears to be related to the different coordination modes of the citrate ligands in the complexes. The ligand exchange reactions show an I_a mechanism for $Al(Cit)_2^{3-}$ and *Sy*. These two complexes are fluxional ($k_{298}^{Sy} = 230$ s^{-1}), the *intra*-molecular rearrangement of *Sy* goes through a bond rupture mechanism. *As* is neither fluxional nor labile for ligand exchange, $k_{As} \leq 0.03$ s^{-1} at 353 K. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Aluminium-citrate complexes; ^{1}H- and ^{13}C-NMR spectroscopy; Ligand exchange

1. Introduction

Aluminium contamination and mobility in the environment has attracted considerable attention in recent times because of the acidification of natural waters and soils arising from acid rain [1]. In humans abnormally

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high aluminium levels have been linked to important pathologies [2]. The solubility and transport of aluminium is greatly increased by complex formation. As a 'hard' metal ion, Al^{3+} has an affinity for 'hard' donors such as O-containing compounds. Such ligands are widely found in geochemical, biological and industrial systems. The tricarboxylic acid anion citrate has particular importance in the bioinorganic chemistry of aluminium [3]. In biological fluids citrate is an effective small molecule of aluminium transport, being the strongest low molecular weight metal binder in blood plasma [4]. It is present in many fruits and fruit drinks and it can interact with package materials (e.g. tin [5], or aluminium). The citrate ion is a key constituent of 'citric acid cycle' and has found application in nuclear medicine [6].

Extensive research has been carried out on the analytical, equilibrium, structural (both in solids and solution) and kinetic aspects of aluminium chemistry [7–16]. The slow kinetics of many Al(III) species plays an important role in the speciation and analytical chemistry of aluminium [1]. For example, the unusual slowness of the formation of $Al(edta)^{-}$ during complexometric titrations necessitates use of a back-titration [17]. Potentiometric studies have demonstrated that the Al(III)-citrate system passes through metastable states, requiring many days to reach true equilibrium [4a,18,19].

Several aspects of Al(III) kinetics have been studied. *Water exchange* (1/*a*) rate between the $Al(H_2O)_6^{3+}$ and the bulk water has been measured by ^{17}O-NMR [20,21]. This process is much faster for $[AlL_x(H_2O)_{6-x}]^{(3-x)+}$ species [22]. A dissociative interchange, I_d, mechanism for water exchange has been suggested from the values of activation volume, $\Delta V^{\#}$. However, *solvent exchange* (1/*b*) processes in non-aqueous solutions (DMSO, DMF, TMPA) [23] have the limiting dissociative mechanism, *D*. *Complex formation* reactions (2) involving Al(III) can be treated by the Eigen–Wilkins formalism [24]. However, there is no general agreement, even for unidentate ligands, as to whether the rate determining step (r.d.s.) is the leaving of a water molecule from the outer sphere complex (*D*) or the replacement of a water molecule by the ligand in a concerted process (I_d or *I*) [25–31]. Systematic studies of complexation reactions between Al(III) and multidentate ligands are scarce, presumably because of the experimental difficulties in studying metastable systems. *Ligand exchange* reactions (3) exhibit mechanisms that depend on the nature of the ligand. For example, dynamic NMR studies of the Al(III)–acac (acetylacetonate) system established an I_d mechanism [32]. Recently, we found substantial differences in the ligand exchange rates of AlF_n^{+3-n} ($n = 1, 2, 3$) complexes and suggested an I_a mechanism [34]. *Stereochemical rearrangements* Eq. (4) involving *intra*-molecular rearrangement of polyatomic organic ligands coordinated to Al(III) (4/*a*) have been studied by ^{1}H- and ^{19}F-NMR in non-aqueous solvents [33]. The rates of terminal CF_3 group exchange in mixed substituted β-diketonates were determined by bond-rupture. A geometric (*cis*/*trans*) *isomerisation* (4/*b*) process has been established for AlF_2^{+} [34] by high field ^{19}F-NMR and was shown to be an *intra*-molecular reaction. An *intra*-molecular isomerisation of *cis*/*trans* $Al(oxalate)_2^{-}$ complexes was detected by ^{13}C-NMR [15].

In spite of the progress to date, there is an obvious need to decrease the gap between the rate of water exchange ($k_w \approx 1\ s^{-1}$, or life time, $\tau_w \approx 1$ s) and the required equilibration time (several hours or days) for chelate-complexes, especially for some polynuclear species [4a,19].

This paper attempts to find a correlation between the kinetic behaviour of citrates in *inter*- and *intra*-molecular exchange reactions and the coordination mode of the ligands in the most important Al-citrate complexes [15], at equilibrium. This avoids the uncertain stoichiometry of the studied reactions and we can safely use the conventional dynamic NMR methods of band shape analysis (T_2 time scale) and magnetization transfer (MT) (T_1 time scale) using ^{1}H- and ^{13}C-NMR spectroscopy.

2. Experimental

2.1. Chemicals

Aluminium chloride solution was prepared from 99.9999% purity Al wire (Ajka, Hungary) as described elsewhere [34]. Sodium citrate ($Na_3Cit \cdot 5H_2O$, where $Cit = C_6H_5O_7^{3-}$) and citric acid (H_3Cit) (Reanal p.a.) were used without further purification. Hydrochloric acid solutions were made by diluting 37% HCl (Merck p.a.) solution and standardized against potassium hydrogen phthalate. Sodium cyanide ($Na^{13}CN$, Cambridge Isotopes) was measured by weight into the samples. Concentrated ($c = 3$ M) NaOH solutions prepared by weight in D_2O were used to adjust pH in concd. Al-citrate samples.

The ammonium salt of $Al_3(H_{-1}Cit)_3(OH)(H_2O)^{4-}$ (where $H_{-1}Cit = C_6H_4O_7^{4-}$) was prepared from $Al(NO_3)_3 \cdot 9H_2O$ as described earlier [35]. The sodium salt was prepared in a similar way: 19.20 g (0.10 mol) solid H_3Cit was dissolved in 87 cm^3 5 M NaOH solution (0.44 mol) and 37.52 g (0.10 mol) $Al(NO_3)_3 \cdot 9H_2O$ was added with vigorous stirring. The resulting clear solution (ca. pH 4.5) was kept 1 h at 353 K, while pH decreased to ca. 2.5. By addition of NaOH pellets the pH was raised to ca. 8 and the solution was stirred for 1 day at room temperature. No precipitation occurred and ^{1}H- and ^{13}C-NMR spectra of this solution were identical with those prepared from the NH_4^{+} salt. After addition of EtOH, precipitation occurred and the slurry was kept

2 days with constant stirring. The precipitate was filtered, washed with 1:1 EtOH–water and dried at 363 K, yield: 80%. The water content was determined by drying samples at 423 K and indicated five waters/complex. ^{1}H- and ^{13}C-NMR spectra of samples prepared from the Na^+ salt were identical again with those of the NH_4^+ salt, and showed no time dependence.

The measured powder X-ray pattern of the Na^+ salt had shown close similarity to the calculated one from the known structure of the NH_4^+ salt.

In this study the Na^+ salt was used, to avoid the buffering capacity of NH_4^+ for the pH dependent studies. To avoid the large ^{1}H-NMR signal of normal water, NMR samples were prepared by dissolution of the weighed solid in D_2O. No time dependence of the spectra was observed. After pH or ligand concentrations were adjusted, samples were equilibrated for at least 1 day prior to the NMR measurements, unless otherwise specified.

2.2. pH measurements

Free hydrogen concentrations, $[H^+]$ were measured by a combined glass electrode (Radiometer), calibrated with pH 4.01 and 6.87 buffer solutions. In D_2O, pD was calculated as pH +0.4 [36]. Some samples were prepared at very high concentrations ($c_{Al} = 0.8$ M) to get good signal to noise ratio in the ^{13}C-NMR, so no constant ionic medium could be kept. In such cases pH values given by potentiometric measurements can be very uncertain because of the liquid junction potential. Therefore, $Na^{13}CN$ ($c_{CN} = 0.01$ M) was added to the solution, and the pH was measured in situ by monitoring the time-averaged ^{13}C-NMR shift (δ) of the $H^{13}CN/^{13}CN^-$ signal. It has been shown that: $pH = pK_{HCN} - \log(\delta_{CN} - \delta)/(\delta - \delta_{HCN})$, where $pK_{HCN} = 10.01$ ($I = 3$ M) and $\delta_{HCN} = 115.35$ and $\delta_{CN} = 167.83$ ppm are, respectively the chemical shift in highly acidic and highly basic samples. This method is sensitive to pH in the range $pK_{HCN} \pm 1.9$ [37a,37b]. Cyano complexes of Al^{3+} have not been reported in aq. solution and therefore no competition with citrate has to be considered.

2.3. NMR measurements

^{1}H-NMR spectra were recorded at 360, 400 and 500 MHz, ^{13}C-NMR spectra were recorded at 90, 100 and 125 MHz with a Bruker AMX360 using a QNP probehead, AM400, DMX500 and DRX500 spectrometers using a 5 mm inverse probehead in locked mode. Typical acquisition parameters for ^{1}H (and ^{13}C)-NMR spectra were: flip angle ca. 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 without decoupling and with power gated or, for quantitative purposes, with the inverse gated decoupling pulse sequence. MT experiments were performed by the DANTE pulse sequence [38a]. The simplest rectangular shaped Dante sequence was used with typically 30–50 pieces 1–1.2 μs long pulses applying ca. 0.5 ms long delays in between. The total pulse length and the selectivity was roughly calculated then tuned experimentally usually achieving 85–95% efficiency for inversion. When studying two signals, MT was made by the method of three hard pulses: $90^\circ_x - \tau_1 - 90^\circ_y - VD - 90^\circ_x - AQ$ [38b]. The temperature of the probe head was checked by the ‘methanol-thermometer method’ [39]. 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. Line width data were evaluated by fitting Lorenz-curves. Line broadening (LB in Hz) of the ^{13}C-NMR signals, being in the ‘slow exchange regime’ on the actual chemical shift time scale, due to the chemical exchange was calculated as $LB = LW^{obs} - LW^0$, where LW^{obs} is the observed line width, and LW^0 is non-exchange line width of the signal, respectively. For all exchanging sites in ^{13}C-NMR LW^0 ca. 1 Hz was obtained in independent experiments. The pseudo first order rate constants were calculated by using the formula $k^{obs} = LB\,\pi$ [40].

2.4. Data treatment

Dynamics in ^{1}H-NMR spectra were analyzed by simulation of measured spectra according to Chan and Reeves [41a] using a home made program written in MATLAB [41b]. The measured and calculated spectra were compared with respect to the line widths, relative intensities and positions of the peaks. The non-exchange line width, the chemical shifts, and the coupling constants were the input parameters. Dynamic ^{13}C-NMR studies were performed by means of inversion transfer experiments. The change in magnetization vector (taken from the integrated intensity of the corresponding signal) is given by:

$$\mathbf{M}_t = \exp(\mathbf{R} \cdot t)(\mathbf{M}_0 - \mathbf{M}_\infty) + \mathbf{M}_\infty \qquad (1)$$

where $\mathbf{M}$ is the column matrix of magnetization on each site at time t, $\mathbf{M}_\infty$ is the column matrix of equilibrium longitudinal magnetization. $\mathbf{R}$ is the square rate matrix with off-diagonal elements, $\mathbf{R}_{ij} = k_{ji}$ (the pseudo first order rate constant from site j to site i), and diagonal elements, $\mathbf{R}_{ij(i=j)} = -(1/T_{1i}) - \Sigma_{i \neq j}\, k_{ij}$. The unknown parameters $\mathbf{M}_\infty$, T_{1i}, k_{ji} were fitted by a non-linear least-square method using the MATLAB program. In some cases T_{1i} values were determined from independent measurements.

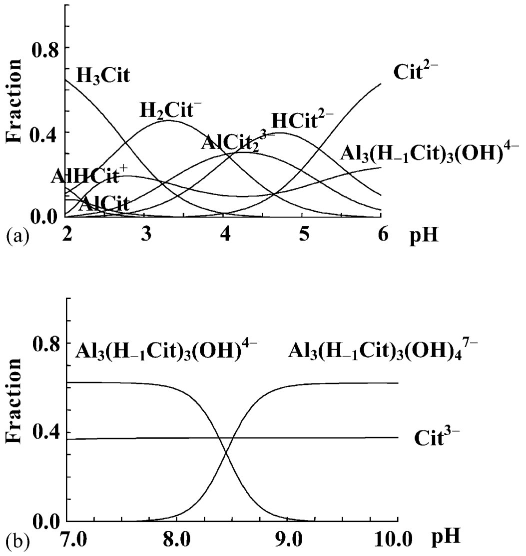


Fig. 1. Typical distribution diagrams (showed for citrate fraction) for $c_{Al} = 0.25$ M and $c_{Cit} = 1.00$ M (a) and for $c_{Al} = 0.5$ M and $c_{Cit} = 0.8$ M (b).

3. Results and discussion

Assignment of the NMR signals to the species identified in Öhman's equilibrium model [18] can be found elsewhere [15]. For pH 3–11, five species are significant: $Al(Cit)_2^{3-}$, $Al_3(H_{-1}Cit)_3OH^{4-}$ $Al_3(H_{-1}Cit)_3(OH)_4^{7-}$ (*Sy*) and free citrate (*Free*, meaning citrate in all its non-complexed forms, H_iCit^{-3+i}, $i = 0–3$ showing always one time averaged peak) giving ^{1}H- and ^{13}C-NMR signals and $Al(OH)_4^-$ (measured by ^{27}Al-NMR, but not used for the dynamics studies). The structurally-related transient species, $Al(Cit_2H_{-1})^{4-}$ and $Al(Cit_2H_{-2})^{5-}$ [42] cannot be detected in our samples. Typical distribution curves are found in Fig. 1. The coordination mode of citrate in the complexes is different both in solid and solution showing bridging (μ and μ_3) tetradentate (*As*) [35] and non-bridging tridentate (the monomeric $Al(Cit)_2^{3-}$ [42] and the trinuclear *Sy* [15]) geometries.

3.1. Inertness of $Al_3(H_{-1}Cit)_3OH^{4-}$ (*As*)

The *As* complex is the major species at pH values ca. 3–8 and total aluminium concentration, $c_{Al} \geq 1$ mM and ratio Al–citrate = 1:1. Both ^{1}H- and ^{13}C-NMR signals of *As* were narrow in the whole pH region in accordance with earlier findings [35]. Surprisingly, no measurable line broadening could be measured up to 80 °C in solutions prepared from Na^+ or NH_4^+ salts of the complex. Thus there is no exchange between the three non-equivalent ligands of *As* on the NMR time scales. If 1 Hz is the measurable exchange broadening ($\Delta\nu_{1/2} \leq 1$ Hz), then $k_{obs} \leq \Delta\nu_{1/2}\pi \leq 3$ s^{-1} or $1/k_{obs} = \tau \geq 0.3$ s for the three different citrate sites of *As*. The longitudinal relaxation time scale may provide a tool to follow slower processes using MT technique. In our case the T_1 values of the citrate ligand are between 2 and 6 s. No MT could be detected in the ^{13}C-NMR spectra up to 80 °C, therefore, $k_{obs} \leq 0.03$ s^{-1} (or $\tau \geq 3–5\ T_1 \approx 30$ s, where τ is the life time at a given site), can be calculated for the *intra*-molecular exchange reactions between the three citrate sites of *As.* The lack of MT even between the two non-equivalent terminal sites of a given citrate ligand means that there is no fluxional site-exchange in *As* within about 30 s.

The non-fluxionality of the bridging tetradentate ligands of *As*, does not imply similar inertness towards *inter*-molecular exchange with a free ligand. Nevertheless, a ^{13}C-NMR MT experiment at 80 °C using a solution of *As* with excess citrate ($c_{As} = 0.30$, $c_{Free} = 0.10$ at pH 4.0) shows, that this *inter*-molecular exchange is also unmeasurably slow, $k_{obs} \leq 0.03$ s^{-1}. Note that this solution was metastable but during the 6 h MT experiment no measurable transformation of *As* to $Al(Cit)_2^{3-}$ was observed.

Table 1
90 megahertz ^{13}C-NMR data of a solution with $c_{Al} = 0.25$ M, $c_{Cit} = 1.0$ M at pH 4.3 at different temperatures

T (K)	Free citrate			$Al(Cit)_2^{3-}$			k_{02}^{obs} (s^{-1})
		δ (ppm)	LW (Hz)		δ (ppm)	LW (Hz)	
298	COO(c)	182.8	1.01	COO(c)	185.22	13.8	1.1 ± 0.9 [a]
	COO(t)	179.4	1.12	COO(t)	179.52	10.1	
	C(q)	77.1	1.59	C(q)	77.24	3.7	
	CH_2x	77.24	1.45	CH_2	45	~ 150	
323[b]	C(q)	77.41	1.56	C(q)	77.65	1.9	2.6 ± 0.4 [a]
348	COO(c)	183.0	5.05	COO(c)	185.35	6.0	14.5 ± 0.3 [a]
	COO(t)	179.8	4.30	COO(t)	180.05	6.5	(12 ± 3) [c]
	C(q)	77.58	4.83	C(q)	77.86	5.5	
	CH_2	48.00	15.62	CH_2	45.66	23.6	

[a] From MT measurements.

[b] Missing values are due to the fact, that spectra were not recorded in the respective region.

[c] $k_{02}^{obs} = LB\ \pi$ from data of this table.

3.2. Dynamics of $Al(Cit)_2^{3-}$ complexes

As stated above, at pH ca. 4 the formation of $Al(Cit)_2^{3-}$ is preferred at high citrate/Al(III). The NMR signals of this complex are broadened at room temperature in contrast to the signals of *Free* (Table 1).

3.2.1. Intra-molecular exchange reaction of $Al(Cit)_2^{3-}$

As just noted (Table 1) the *Free* signals at room temperature show their natural line width while those of $Al(Cit)_2^{3-}$ are broad. This is consistent with an *intra*-molecular exchange process for the complex. The $Al(Cit)_2^{3-}$ signals narrow at higher temperatures, typical for time-averaged signals in the 'fast exchange regime' but the extent of broadening for the various peaks differ (Table 1). Following Matzapetakis *et al.* [42], we believe that the three 1:2 complexes, $Al(Cit_2H_{-2})^{5-}$, $Al(Cit_2H_{-1})^{4-}$ (not present at our experimental conditions) and $Al(Cit)_2^{3-}$ are structurally similar, differing only in the number (0, 1 or 2, respectively) of protonated carboxylate groups. In $Al(Cit)_2^{3-}$ both citrates coordinate via the deprotonated OH, the central $-COO^-$ and one terminal $-COO^-$, while the other terminal $-COO^-$ is unbound and protonated. The fluxionality probably corresponds to the simultaneous replacement of the coordinated terminal $-COO^-$ group of one ligand by the non-coordinated terminal $-COO^-$ group of another. This rearrangement involves opening and closing two six-membered chelate rings, but the two five-membered chelate rings remain unchanged, as has recently been suggested [42] for $Al(Cit_2H_{-2})^{5-}$. This model is supported by the large broadening of the $-CH_2-$ carbon signal and the smaller broadening of the quaternary carbon.

3.2.2. Inter-molecular exchange reaction of $Al(Cit)_2^{3-}$

The *inter*-molecular exchange reaction between *Free* and $Al(Cit)_2^{3-}$

$$Al(Cit)_2^{3-} + {}^*Cit \underset{k_{0,2}}{\overset{k_{2,0}}{\rightleftharpoons}} Al(Cit)({}^*Cit)^{3-} + Cit \qquad (2)$$

was studied by ^{13}C-NMR at $c_{Al} = 0.25$ M, $c_{Cit} = 1.0$ M and pH 4.0, where these two species are dominant and little *As* is formed. Note that as *Free* is present in different protonated forms at this pH, charges are omitted.

MT experiments were performed in the quaternary carbon region because the other peaks were too broad. Inverting the *Free* signal (77.09 ppm) at 298 K resulted in only a small decrease in the intensity of $Al(Cit)_2^{3-}$ (77.14 ppm) at a delay time of ca. 0.5 s. This exchange increases with temperature, so that at 348 K negative magnetization was transferred with a delay of only 0.06 s. Integration of the peaks at each delay time gives the plot shown in Fig. 2. The k_{02}^{obs} values calculated from these data are given in the last column of Table 1. As $Al(Cit)_2^{3-}$ is detectable only over a narrow pH range with a large excess of *Free*, it is not possible to determine the complete rate equation.

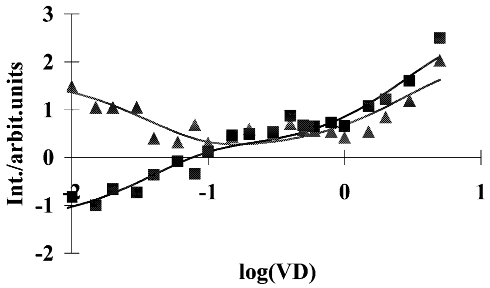


Fig. 2. Intensity of 90 MHz ^{13}C-NMR signals in arbitrary units vs. logarithm of the variable delay time (s) in a sample of $c_{Al} = 0.25$ M, $c_{Cit} = 1.0$ M at pH 4.3 at 348 K. Continuous lines represent fitted curves with $k_{02}^{obs} = 15$ s^{-1}, while symbols, *Free* (■) and $Al(Cit)_2^{3-}$ (▲) correspond to measured values. MT was performed by three hard pulses.

Comparing $k_{02}^{obs} = 15 \pm 3$ s^{-1}, measured at 348 K, with the upper limit of the rate constant for the *As* complex ($k_{obs} \leq 0.03$ s^{-1}), estimated at 353 K, the difference is at least three orders of magnitude. Thus, it is not surprising that the non-bridging tridentate citrate ligands of $Al(Cit)_2^{3-}$ are much more labile towards ligand exchange than the bridging tetradentate ligands of *As*. The lability for $Al(Cit)_2^{3-}$ is six or seven orders of magnitude higher than that of $Al(acac)_3$ in organic solvents (Table 3), although comparisons between different solvents must be made with care.

The activation parameters of the *inter*-molecular exchange can be estimated as follows. Using the measured constant, k_{02}^{obs}, the rate equation is of the form:

$$v = k_{02}^{obs}\,[Cit] \qquad (3)$$

Since the true rate equation is not known, a good starting point is:

$$v = k_{02}\,[Al(Cit)_2^{3-}]\,[Cit]^x \qquad (4)$$

Table 2
Pseudo first order rate constant values obtained for *intra*- and *inter*-molecular exchange reactions of *Sy* at different temperatures, and the corresponding measured 500 MHz ^{1}H-NMR line width values

T (K)	k_{intra}^{obs} (s^{-1})	k_{03}^{obs} (s^{-1})	LW (*Free*) (Hz)	LW (*Sy*) (Hz)
273	–	0	1.1	– [a]
285	80	0	1.1	– [a]
298	200	0	1.1	– [a]
315	822	0	1.1	4.7
325	2.80×10^3	1.1	3.1	3.1
345	1.50×10^4	2.7	6.0	4.1
355	1.50×10^4	3.7	7.0	5.2

[a] Missing values are due to the fact that the correct broadenings can not be measured at those temperatures, because the signals are at coalescence.

Table 3
Activation parameters of exchange reactions together with selected literature values

Complex/type of exchange reaction	Solvent	ΔH^* (kJ mol^{-1})	ΔS^* (J mol^{-1} K^{-1})	k_{298} (s^{-1})	Mechanism	Reference
$Al(H_2O)_6^{3+}$/solvent exchange	Water	85	+42	1.29	D/I_d	[21]
$Al(acac)_2(hfac)$/*intra*-molecular rearrangement	CH_2Cl_2	(90) [b]	(+45) [a]	0.86	Bond-rupture	[33]
$Al(acac)_3$/*inter*-molecular ligand exchange	Hacac	85	−38	9.1×10^{-5}	I_a	[32]
$Al(tfac)_3$/*intra*-molecular site exchange	$CDCl_3$	114	+68	0.65 at 358 K	Bond-rupture	[44]
As/*inter*-molecular ligand exchange	Water	–	–	< 0.03 [b]	–	This work
As/*intra*-molecular ster. rearrangement	Water	–	–	< 0.03 [b]	–	This work
$Al(Cit)_2$/*inter*-molecular ligand exchange	Water	43 ± 1	-90 ± 29	1.0 ± 0.1	I_a	This work
Sy/water assisted *inter*-molecular ligand exchange	Water	65 ± 7	-78 ± 21	0.08 ± 00.01	I_a	This work
Sy/*intra*-molecular rearrangement	Water	70 ± 5	$+34 \pm 15$	230	Bond-rupture	This work
$Al(Ox)_3^{3-}$/*inter*-molecular ligand exchange	Water	164 ± 17	225 ± 51	$6 \pm 1 \times 10^{-6}$	D	[15]
$Al(Ox)_2^{-}$/*intra*-molecular *cis–trans*	Water	67 ± 5	-6 ± 6	5 ± 0.5	Bond-rupture	[15]
AlF^{2+}/*inter*-molecular ligand exchange	Water	–	–	$< 2 \times 10^3$	I_a	[34]
AlF_2^{+}/*inter*-molecular ligand exchange	Water	–	–	1.5×10^6	I_a	[34]
AlF_3/*inter*-molecular ligand exchange	Water	–	–	1.3×10^7	I_a	[34]

[a] Values in parentheses mean Arrhenius activation energies.
[b] $k_{353\ K} < 0.03$ s^{-1}.

from which the pseudo first order rate constant is:

$$k_{02}^{obs} = k_{02}\ [Al(Cit)_2^{3-}]\ [Cit]^{(x-1)} \tag{5}$$

where k_{02} is the real rate constant and x is the reaction order of Cit, with likely values of 0 and 1.

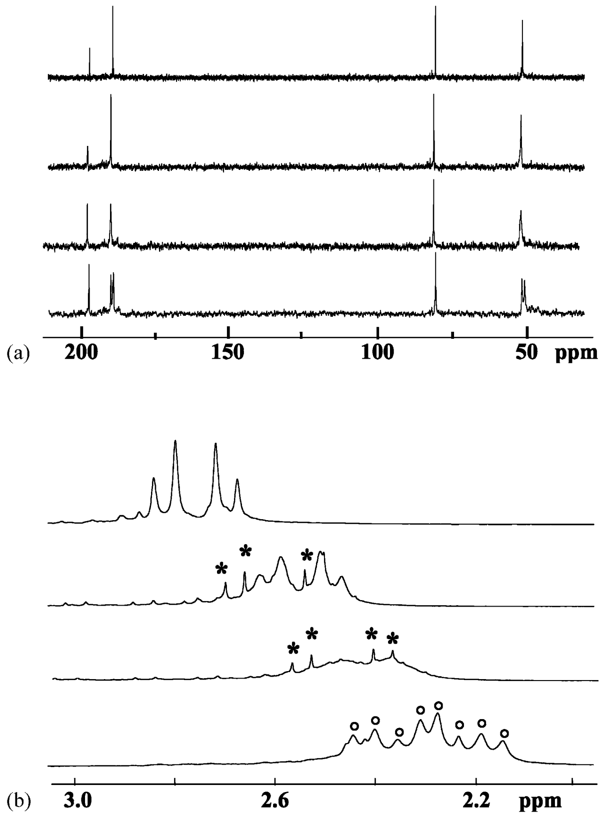


Fig. 3. 100 megahertz ^{13}C- (a) and 400 MHz ^1H- (b) NMR spectra of *Sy* in a solution with $c_{Al} = c_{Cit} = 0.75$ M at pH 9 at different temperatures (K): 323, 300, 278 and 263 from top to bottom spectra. (The small narrow signals, *, belong to free citrate, $A'B'$ and $A''B''$ are labelled with °, respectively.)

The dependence of the pseudo first order rate constant on temperature is given by the Eyring-relation:

$$\ln\frac{k_{02}^{obs}}{T} = \ln\frac{k_B}{h} + \frac{\Delta S^*}{R} + \ln[Al(Cit)_2^{3-}] + (x-1)\ln[Cit] - \frac{\Delta H^*}{RT} \tag{6}$$

where k_B, h and R are, respectively the Boltzmann, Planck and universal gas constants. If the likely values of x and the concentrations of $Al(Cit)_2^{3-}$ and Cit (obtained from the ^{13}C-NMR spectra) are used a plot of $\ln(k_{02}^{obs}/T)$ against $1/T$ gives $\Delta H^* = 43 \pm 1$ kJ mol^{-1}, with $\Delta S^* = -96 \pm 29$ J mol^{-1} K^{-1} for $x = 0$ and $\Delta S^* = -90 \pm 29$ J mol^{-1} K^{-1} for $x = 1$. Although ΔS^* has a large uncertainty because of the long extrapolation of $1/T$ to zero, these values indicate a definite loss of entropy during the formation of the transition state, irrespective of whether $x = 0$, or 1. If $x = 0$, the rate is independent of the free citrate concentration and a dissociative mechanism could be operative. However, this seems unlikely given the observed loss of entropy and the relatively small ΔH^*. Another possibility corresponding to $x = 0$ is a so-called water assisted I_a mechanism. Alternatively, these activation parameters are also consistent with an associative mechanism, probably I_a, with $x = 1$. Further work is clearly necessary to resolve these issues but it is possibly noteworthy that an I_a mechanism has been proposed [32] for the *inter*-molecular ligand exchange reaction of $Al(acac)_3$ in organic solvents, where the activation parameters are $\Delta H^* = 85$ kJ mol^{-1} and $\Delta S^* = -38$ J mol^{-1} K^{-1}, $\Delta V^* = +10$ cm^3 mol^{-1}.

3.3. *Dynamics of* $Al_3(H_{-1}Cit)_3(OH)_4^{7-}$ *(Sy)*

By increasing the pH, the trinuclear complex *As* can be transformed into an other trimer, $Al_3(H_{-1}Cit)_3(OH)_4^{7-}$ (*Sy*). This reaction has been shown previously to be very slow requiring up to 1 week for equilibration [18], presumably due to the major change in the structure. The addition of three equivalents NaOH to *As* resulted in the formation of an $Al_3(OH)_4^{5+}$ core. The three citrate ligands were each coordinated to one Al(III) with a deprotonated hydroxyl oxygen and two terminal carboxylates in the inner sphere and the deprotonated central carboxylate unbound [15] in accordance with the tentative structure proposed by Öhman [18].

3.4. *Intra-molecular exchange*

^{1}H- and ^{13}C-NMR signals of *Sy* are substantially broadened compared to those of *As* and/or *Free*, which coexist in the equilibrium system. This kind of broadening can be attributed to an *intra*-molecular rearrangement of *Sy*, analogous to that of $Al(Cit)_2^{3-}$ mentioned above.

The ^{13}C-NMR spectra (Fig. 3a) show that the broadening at room temperature is substantial for the carbon signal of the $-CH_2-$ (50 ppm) and terminal –COO groups (182 ppm), less pronounced for the central –COO group (190 ppm) and negligible for the quaternary carbon signal (75 ppm). At lower temperature ($T \leq 270$ K) the signals of $-CH_2-$ and the terminal –COO groups are split. ^{1}H-NMR spectra (Fig. 3b) behave similarly, at $T \leq 270$ K the broad *AB* type signal is split into two sets of signals, *A′B′* and *A″B″* (represented in figure with o). These spectral changes indicate that the two $-CH_2-COO$ arms of the three citrate ligands in *Sy* become non-equivalent at lower temperatures, but the overall symmetry remains. The symmetry could be distorted further at even lower temperature, as it is indicated by the appearance of three peaks of the terminal –COO groups, see Fig. 3a, button trace. The split signals at 263 K indicate non-equivalency of the $-CH_2-COO$ arms.

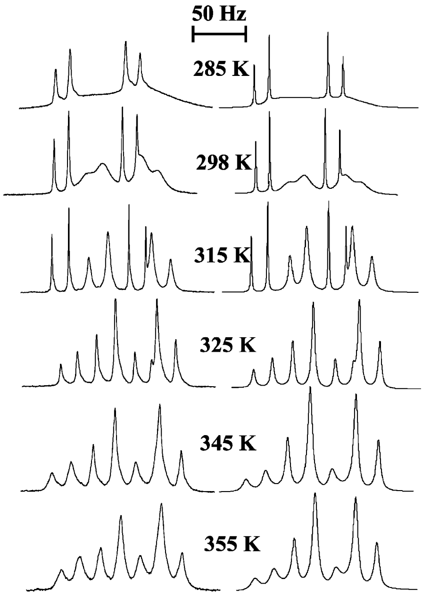
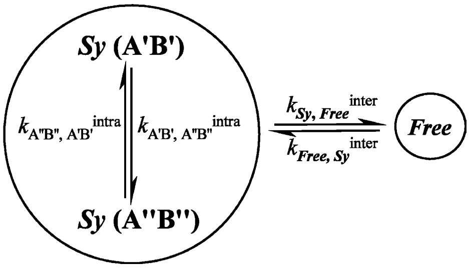


Fig. 4. Recorded (left) and simulated (right) 500 MHz ^{1}H-NMR spectra of *Sy* and *Free* in a solution with $c_{Al} = c_{Cit} = 0.23$ M at pH 10.7 at different temperatures.

The dynamics of *Sy* was studied quantitatively by ^{1}H-NMR (Fig. 4). A variable temperature study was performed on a sample with $c_{Al} = c_{Cit} = 0.23$ M at pH 10.7, where the *Sy*–*Free* = 7:3. The ^{1}H-NMR spectrum of this solution consists of a pair of asymmetric doublets of *Free* (AB_{FREE}, narrow) and *Sy* (broad, time-averaged AB_{SY}). It is presumed that the broadening of the *Sy* signals is caused by rearrangement between the two limiting conformations of the $-CH_2-COO$ arms, both showing a pair of asymmetric doublets, *A′B′* and *A″B″*. *Inter*-molecular ligand exchange between *Sy* and *Free* is also expected to occur. Thus, for the simulation of the spectra a 12-site system has to be considered. Two pseudo first order rate constants are introduced: k_{03}^{obs} for *inter*-molecular exchange, and k_{intra}^{obs} for *intra*-molecular exchange. These processes are represented in Scheme 1.

Analyzing the spectra of Fig. 4, it can be seen that at $T \leq 315$ K the signal of *Free* (AB_{FREE}) shows its natural line width of ca. 1 Hz, indicating only the *intra*-molecular exchange is operative. *Sy* gives a pair of asymmetric doublets, AB_{Sy}, at 315 K. Broadening of this signal starts at 298 K and coalescence is attained at 285 K. (The separation into the asymmetric doublets is hardly detectable in Fig. 4 as this diluted solution freezes at lower temperatures. The splitting was detected in more concentrated samples at $T \leq 270$ K, see Fig. 3. From these spectra the chemical shifts of signals *A′B′* and *A″B″* can be determined. These values were used as input parameters for the simulation.) The change of chemical shift with temperature was taken into account by a linear approximation. Populations of *A′B′* and *A″B″* were set equal. The values of the rate constants were varied so as to obtain simulated spectra with the same characteristics as the measured spectra. The fast exchange regime for the *intra*-molecular exchange is reached at $T \geq 315$ K and the averaged signal, AB_{Sy},



Scheme 1.

narrows. Besides this rearrangement, exchange between the bound and free citrate begins, and a value for $k_{03}^{\mathrm{obs}} \neq 0$ has been fitted. As a consequence, a broadening appears on the free citrate signals, which contributes to the broadening of the AB_{Sy} signal. At 355 K the fitted value for $k_{\mathrm{intra}}^{\mathrm{obs}}$ is the same as at 345 K, indicating that the *intra*-molecular exchange becomes too fast to be observed. The line width at 355 K is determined by the *inter*-molecular exchange, with $k_{03}^{\mathrm{obs}} = 3.7\ \mathrm{s}^{-1}$. The data is summarized in Table 2.

The values of the rate constants at different temperatures can be used for calculation of the activation parameters. In the case of $k_{\mathrm{intra}}^{\mathrm{obs}}$, the activation parameters are: $\Delta H^* = 70 \pm 5$ kJ mol^{-1} and $\Delta S^* = 35 \pm 15$ J mol^{-1} K^{-1}. The value of ΔS^* does not differ greatly from zero, as is normal for a purely *intra*-molecular exchange process. Energy barriers of fluxional processes are better expressed in terms of ΔG^*. The value at 300 K is $\Delta G^* = 59.4$ kJ mol^{-1}. This is slightly over the middle of the wide range, $\Delta G^* = 5$–100 kJ mol^{-1}, reported in the literature [43] for fluxional rearrangements.

It is difficult to rationalize this rearrangement, because we do not know the structure of the conformers. (Attempts to crystallize this complex failed.) Detailed study of the symmetry is out of the scope of this work. However, several conformers of *Sy*, differing with respect to the conformation of the possible six chelate rings, can be drawn. The two $-\mathrm{CH_2}-\mathrm{COO}^-$ groups of one citrate in *Sy* could have two conformations that might be non-equivalent at low temperatures. Values of $\Delta H^* = 114$ kJ mol^{-1} and $\Delta S^* = 68$ J mol^{-1} K^{-1}, have been reported for fluxional site exchange of $\mathrm{Al(tfac)_3}$ (tfac = trifluor-acetylacetonate) [44] in $\mathrm{CDCl_3}$, see Table 3. The relatively large ΔG^* in our case might suggest that this stereochemical rearrangement is going via a bond-rupture mechanism, in which one Al(III)–oxygen bond (of the nine ligand O-donors coordinated to the $\mathrm{Al_3(OH)_4}$ core) ruptures to give a five-coordinate intermediate at one Al center. We believe, that the hydroxyl oxygens acting as anchor donors remain coordinated, whilst one of the terminal carboxylate groups leaves the coordination sphere of Al(III). Following this r.d.s., the complete fluxional rearrangement, involving all six $-\mathrm{CH_2}-\mathrm{COO}$ arms of *Sy* happens simultaneously, or in relatively fast consecutive steps. A similar mechanism has been proposed for mixed Al(III)-β-diketonate complexes [33].

3.5. *Inter-molecular ligand exchange reaction of Sy*

The inter-molecular exchange has already been discussed briefly in relation to the analysis of the ^{1}H-NMR spectra. It was undetectably slow at room temperature and so the MT technique using ^{13}C-NMR was applied. The exchange reaction is:

$$\mathrm{Al_3(H_{-1}Cit)_3(OH)_4^{7-}} + {}^*\mathrm{Cit}^{3-} \underset{k_{0,3}}{\overset{k_{3,0}}{\rightleftharpoons}} \mathrm{Al_3(H_{-1}Cit)_2({}^*H_{-1}Cit)(OH)_4^{7-}} + \mathrm{Cit}^{3-} \qquad (7)$$

The MT experiment was performed on a sample with $c_{\mathrm{Al}} = 0.80$ M, $c_{\mathrm{Cit}} = 1.38$ M at pH 8.7 and $T = 298$ K where the species *As*, *Sy* and *Free* are present. The central –COO signal of *Sy* was selectively inverted. Typical results are shown in Fig. 5.

An almost unobservable negative magnetization was transferred to the *Free* resonance at 184.8 ppm with a delay time around 3 s (spectra 5th–3rd from the top in Fig. 5). No MT was observed to any of the three –COO(c) on *As*, at 185.39, 180.69 or 180.95 ppm. The *inter*-molecular exchange rate between *Sy* and *Free* was found to be independent of c_{Cit}, c_{Al} and dependent of [H$^+$]. The lack of contribution of a bimolecular reaction between the −7-charged *Sy* and the −3-charged free citrate is consistent with the large electrostatic repulsion that would be expected between these species, and the saturated coordination sphere of the Al(III) centers in *Sy*. A plot of the pseudo first order rate constant against [OH$^-$] is shown in Fig. 6. The expression for the pseudo first order rate constant is:

$$k_{30}^{\mathrm{obs}} = (1/[Sy])\,\mathrm{d}[Sy]/\mathrm{d}t = k_1 + k_2\,[\mathrm{OH}^-] \qquad (8)$$

where $k_1 = 0.08 \pm 0.01$ s^{-1} and $k_2 = 59 \pm 10$ M^{-1} s^{-1}. The rate equation is:

$$v = k_1[Sy] + k_2[Sy]\,[\mathrm{OH}^-] \qquad (9)$$

This two-term rate equation for the *inter*-molecular ligand exchange can be explained by the existence of two parallel processes: (a) a non-hydroxide-catalyzed dissociation of coordinated citrate; and (b) a second order, hydroxide-catalyzed reaction. This kind of ligand exchange reaction for Al-complexes does not appear to have been described previously, although similar phenomena were observed for bismuth-citrate in basic solutions [45–48].

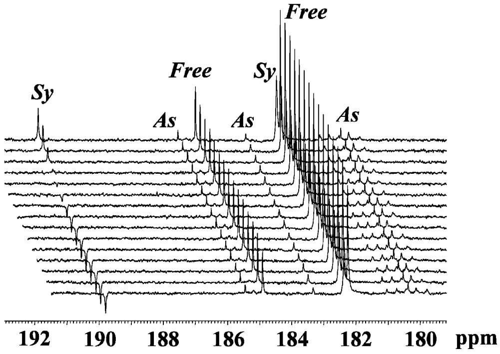


Fig. 5. 90 megahertz ^{13}C-NMR serial plot of the –COO region in a sample with $c_{\mathrm{Al}} = 0.80$ M, $c_{\mathrm{Cit}} = 1.38$ M at pH 8.7 and $T = 298$ K. Variable delays from the bottom to the top are: 0.001, 0.005, 0.01, 0.05, 0.1, 0.2, 0.4, 0.6, 1.0, 1.5, 2.0, 3.0, 5.0, 10.0, 20.0 s. The –COO(*c*) peak of *Sy* has been inverted, using a DANTE pulse train.

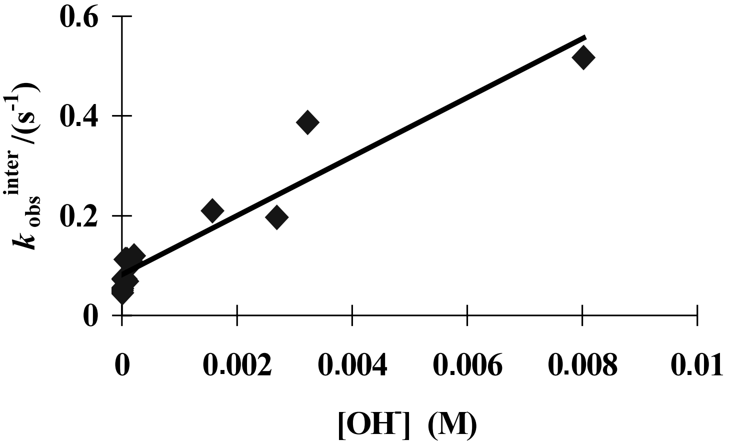


Fig. 6. Graphical representation of the k_{30}^{obs} values obtained from MT experiments as a function of [OH$^-$]. Dots represent measured points, and the continuous line is the fitted curve ($R^2 = 0.9064$).

The variation of k_{30}^{obs} with temperature, based on four measured points (three from ^{1}H-NMR, Table 2, at pH 10.7, and one from ^{13}C-NMR MT, at pH 8.7) over a 57 K interval gives $\Delta H^* = 55 \pm 7$ kJ mol^{-1} and $\Delta S^* = -78 \pm 21$ J mol^{-1} K^{-1}. Based on these values, the proposed mechanism can be considered in two steps:

(a) For the $v = k_1[\mathrm{Sy}]$ first order path, a pure dissociative (*D*) mechanism has to be valid. The r.d.s. involves the formation of *Sy**, followed by a fast citrate exchange:

$$Sy \overset{\text{r.d.s.}}{\rightarrow} Sy^{\#}$$
$$Sy^{\#} + \mathrm{Cit}^* \overset{\text{fast}}{\rightleftharpoons} Sy + \mathrm{Cit}$$

The nature of the complex $Sy^{\#}$ can be clarified by consideration of ΔS^*.

i) $Sy^{\#}$ is a complex with only two coordinated citrates. This is unlikely, since for a reaction of the type: $\mathrm{Al_3(OH)_4(H_{-1}Cit)_3 \rightarrow Al_3(OH)_4(H_{-1}Cit)_2 + Cit}$, the value of ΔS^* should be positive.
ii) If an *I* mechanism is operative, a second order rate equation should have been obtained. This can be explained only by the intervention of a H_2O molecule, which entering into *Sy* results a more ordered transition state for $Sy^{\#}$:

$$\mathrm{Al_3(OH)_4(H_{-1}Cit)_3 + H_2O} \rightarrow [\mathrm{Al_3(OH)_4(H_{-1}Cit)_3,\ H_2O}]^{\#}$$

iii) Something between (i) and (ii). In the r.d.s., one coordinative bond is ruptured and a H_2O molecule enters the vacated place. This new species ($Sy^{\#}$) is more hydrated, corresponding to a decrease in entropy. In the second step the labilized citrate will exchange rapidly. The presented argument leads to the conclusion that water assisted dissociation of the coordinated citrate is happening.

(b) The contribution of the second order process exceeds the first order path only at $[\mathrm{OH^-}] > 2 \times 10^{-3}$ M, i.e. pH > 11.3. (Therefore the activation parameters relate dominantly to the first order path, see above.) At high pH values, even with an excess of citrate over Al(III), the equilibrium shifts towards the formation of $\mathrm{Al(OH)_4^-}$. It seems that a hydroxide attack on the $\mathrm{Al_3(OH)_4}$-core of *Sy* speeds up the ligand exchange reaction substantially. In the (tentative) structure of *Sy*, all three aluminium ions are coordinated by three μ- and one μ$_3$-OH$^-$ groups. Therefore, reaction of any of the Al centers with an additional OH$^-$ could result in the formation of an $\mathrm{Al(OH)_4}$ unit in the intermediate. If this $\mathrm{Al(OH)_4}$ unit leaves the intermediate (because of the very high stability of $\mathrm{Al(OH)_4^-}$), the rest of *Sy* would decompose in one or several fast elementary step(s). The overall reaction can be written as:

$$\mathrm{Al_3(H_{-1}Cit)_3(OH)_4^{7-} + OH^- + H_2O}$$
$$\rightleftharpoons \mathrm{Al(OH)_4^- + 2Al(H_{-1}Cit)OH^{2-} + Cit^{3-}}$$

Interestingly, the mixed hydroxo-complex, $\mathrm{Al(H_{-1}Cit)OH^{2-}}$ (identified at equilibrium by pH potentiometry and a major species in diluted solution around the physiological pH), is present in our concentrated samples only as a minor species over a narrow pH range, just before all Al(III) is converted from *Sy* to $\mathrm{Al(OH)_4^-}$. It is worth mentioning that the transformation of *Sy* to $\mathrm{Al(OH)_4^-}$ is much faster than that of *As* to *Sy*: not more than a few minutes are needed for equilibration.

The values of the activation parameters for the intermolecular ligand exchange of *Sy* are similar to the corresponding data for $\mathrm{Al(Cit)_2^{3-}}$ and $\mathrm{Al(acac)_3}$ (see above). That is, the very large decrease of entropy supports a water-assisted I_a mechanism for the dissociation of *Sy*.

4. Concluding remarks

Comparable kinetic parameters for other aluminium complexes are collected in Table 3. It is interesting to compare the labilities of *Sy*, *As* and $Al(Cit)_2^{3-}$ towards ligand exchange with free ligand using the pseudo first order rate constants. These constants can be used instead of the real first order values because: (i) they should not include a significant contribution from proton-assisted dissociation as the ligands in *As* do not have any unbound site for proton attacks, and the unbound donor sites in $Al(Cit)_2^{3-}$ are already protonated; (ii) no dependence of these constants on the ligand concentration has been observed. In contrast, there are two paths for the ligand exchange of *Sy*, see Eq. (8). Obviously, the rate constant of the water-assisted monomolecular dissociation (k_1) of *Sy* is suitable for comparison with the k_{02}^{obs} and $k_{As,Free}^{obs}$ values of $Al(Cit)_2^{3-}$ and *As*, respectively. The values at 298 K for $Al(Cit)_2^{3-}$, *Sy* and *As* are 1.1 ± 0.1, 0.08 ± 0.01 and < 0.03 s^{-1}, respectively. Using these constants the labilities can be ordered as follows: $Al(Cit)_2^{3-} > Sy \gg As$. (The last inequality is based on the fact that $k_{As} \leq 0.03$ s^{-1} at 353 K.) An I_a mechanism is suggested for both $Al(Cit)_2^{3-}$ and *Sy* complexes from the negative entropy of activation. The rate of *intra*-molecular dynamics of the complexes shows the same tendency.

Can these differences be attributed to the different chemical surroundings at the metal centers or to the different coordination modes of the ligands in the three complexes? The environment of the Al(III) in *As*, having three alcoholic and one hydroxide μ-O donors in an asymmetric core, differs from the other two complexes. *Sy* has the central Al(III) in an $Al_3(OH)_4^{5+}$ core with three μ- and one μ_3-OH^- groups, and the monomer $Al(Cit)_2^{3-}$ has only two equivalent tridentate citrate ligands bound to Al(III). There are not enough experimental data to decide unequivocally if the differences in the quality of neighbouring donor sites in the inner spheres of the Al(III) have any significant influence on the lability of the (other) coordinated citrate ligand(s). Given that all the donors are oxygens, this influence might not be very important. Using this rough simplification, we can consider a relation between the difference of the coordination mode and the lability of the ligand in the individual complexes. It is obvious, that the bridging μ- and μ_3-citrates of *As* are very inert to substitution. The lability of tridentate citrates of $Al(Cit)_2^{3-}$ and *Sy* seems to be affected by the protonation of the unbound carboxyl groups: the ligands, protonated at the unbound terminal carboxylate group in $Al(Cit)_2^{3-}$ are more labile than the deprotonated ones in *Sy*. At the same time there is a hydroxide-catalysed dissociation of the ligands in *Sy*.

The gap between the time scale of ligand exchange reactions and the formation kinetics of *As* (tens of seconds) and *Sy* (hours or days) is very large. Recent studies have clarified some important details of the trimer formation [19]. What is clear, is that the rate of the formation reactions is not determined by the water exchange rate of $Al(ligand)(H_2O)_x$. Rather, the rate of chelate ring formation may be sterically controlled [24] even for the monomeric citrate species. The formation of the trimers is obviously a multistep process. As there is no indication of dimer formation on the macroscopic scale [18], one may conclude, that these intermediates are formed at low concentrations in fast pre-equilibria. The rate-determining step might be the oligomerization. Considering the extremely slow formation of the trimers, the high stability of these species requires a very slow dissociation of these complexes. Our results, the unmeasurably slow ligand exchange for the *As* and the quite slow reaction for *Sy* are in accordance with this condition.

Acknowledgements

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(b) The scheme is: $90^\circ_x - \tau_1 - 90^\circ_y - \mathrm{VD} - 90^\circ_x$, where the subscripts denote the phase of the exciting pulse. The offset is put perfectly in the middle of the chemical shifts of the two peaks. $\tau_1 = 1/(\Delta\nu 4)$, where $\Delta\nu$ is the difference in chemical shift in Hz. This sequence works as follows: the first pulse creates coherence, rotates the equilibrium magnetization to the y-axis. The transverse magnetization of one of the peaks goes to the x-axis during τ_1, while the other goes to the $-x$-axis, the peaks are labeled by their chemical shifts. The second 90° pulse rotates the magnetization in $-x$ to $-z$ and the other one in $+x$ to $+z$ (the selective 180° pulse was composed from two hard 90° pulses similarly to the 2D NOESY sequence). During the VD variable delay the longitudinal relaxation and the exchange proceeds (mixing time), then the third 90° pulse reads the state of the system. The next transient starts after the complete relaxation. The required time was carefully checked experimentally.

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