

# A Raman study on the coordination sites and stability of the [Al(formamide)<sub>5</sub>]Cl<sub>3</sub> complex

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## ABSTRACT

Raman experiments of aluminum chloride and formamide (FA) solutions in different compositions and temperatures were carried out. Spectral changes provoked by the increase of the salt concentration were observed in different regions. The  $\nu_{\text{CO}}$  and  $\nu_{\text{CN}}$  modes of FA upon complexation were upshifted and suggest that the  $\text{—CONH—}$  hybrid (II) is stabilized by Al(III). Bands at 547 and 295  $\text{cm}^{-1}$ , which are assigned to the  $\nu_{\text{AlO}}$  and  $\nu_{\text{AlN}}$  vibrations, respectively, evidence coordination through both O and N atoms of FA. The quantitative analysis performed at the carbonyl stretching region found 5 FA molecules around this cation, resulting in the formation of the  $[\text{Al}(\text{FA})_5]\text{Cl}_3$  complex. Its stability is maintained by whole studied concentration range and up to around 100 °C. At higher temperatures, distortions in the FA shell begin occurring and a new component at 356  $\text{cm}^{-1}$  is then observed and assigned to the  $[\text{AlCl}_4]^-$  complex.

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## 1. Introduction

Our laboratory has recently employed vibrational spectroscopy to investigate two formamide (FA) structures that may be directly related to the catalytic potential of some metal complexes toward hydrolysis of a peptide bond [1–5]. The main idea is to monitor the  $\nu_{\text{CO}}$  and  $\nu_{\text{CN}}$  modes of FA upon complexation. For example, Zn(II), Ni(II) and Mg(II) cause downshifts of the former mode whereas upshifts are observed for the second vibration, suggesting the preferential formation of the  $\text{—C—ON}^+\text{H—}$  hybrid (I). On the other hand, Li(I) and Ca(II) shift both  $\nu_{\text{CO}}$  and  $\nu_{\text{CN}}$  modes to higher wavenumbers and this strongly indicates that the  $\text{—CONH—}$  hybrid (II) is dominant. The stabilization of each FA structure seems to be due to the relative size of the ions. That is, metals of the first transition series (and Mg(II) at this case) have ionic radii close to each other whereas those reported for Li(I) and Ca(II) are completely out of this range [6]. In those works, the polarization provoked by the ions to the O and N atoms of FA has not been enough to provide any bands related to metal–ligand vibrations so that information obtained at the low wavenumber region would be very useful to assure the interpretation given so far for the sites involved in the coordination process.

Al(III) is a good candidate for this kind of study not only because of its biological function [6], but also due to its small size and higher oxidation state. These two latter properties may lead to stronger electrostatic interactions with FA molecules and enable

us to observe bands at low wavenumbers. Furthermore, the solvates formed in solutions of aluminum chloride ( $\text{AlCl}_3$ ) show large dependence on the dielectric constant ( $\epsilon_{\text{R}}$ ), polarity ( $\mu_{\text{S}}$ ) and donor number (DN) of the solvent. For instance, we have shown that in tetrahydrofuran (THF) the  $[\text{AlCl}_3(\text{THF})_3]$  complex is more abundant than  $[\text{AlCl}_4]^-$  and this is mainly due to the low  $\epsilon_{\text{R}}$  and  $\mu_{\text{S}}$  values of THF, which must favor to the neutral species [7]. On the other hand as acetonitrile (ACN), which has higher  $\epsilon_{\text{R}}$  and  $\mu_{\text{S}}$  values, is used  $[\text{AlCl}(\text{ACN})_5]^{2+}$  and  $[\text{AlCl}_4]^-$  are the major ions [8,9] and similar conclusions were also reached by other authors [10] who showed that the integrity of the Al–Cl bond is still maintained even in systems with appreciable amounts of water. In this sense, the  $\text{AlCl}_3/\text{FA}$  system may provide new insights concerning the solvation structures since FA presents the highest values of  $\epsilon_{\text{R}}$ ,  $\mu_{\text{S}}$  and DN, as can be seen in Table 1.

In this work, we present a Raman study of the  $\text{AlCl}_3/\text{FA}$  system in different compositions and temperatures, and our goals are: (i) to monitor the  $\nu_{\text{CO}}$  and  $\nu_{\text{CN}}$  modes of FA coordinated to Al(III) in order to determine which resonance hybrid is stabilized by the metal; (ii) to look for new bands at the region characteristic of the metal–ligand vibrations aiming to better interpret the participation of the coordination sites; (iii) to quantify the average number of FA molecules around this cation and evaluate the stability of the solvate at extremely high temperatures.

## 2. Methods

FA (Vetec) and  $\text{AlCl}_3$  (Sigma–Aldrich) were used without further purification and all solutions were prepared by weight so that the concentrations are expressed as molalities ( $\text{mol kg}^{-1}$ ). Raman

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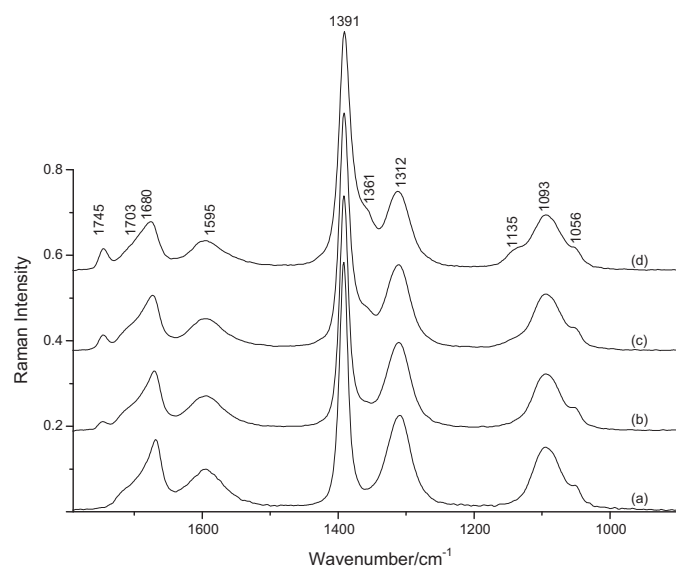
**Table 1**  
Properties of some solvents at 25 °C.

Solvent	$\epsilon_R$	$\mu_S$ (D)	DN (kcal mol <sup>-1</sup> )
THF	7.6	1.6	20
ACN	37.5	3.9	14.1
Water	78.3	1.8	18
FA	111	3.8	24

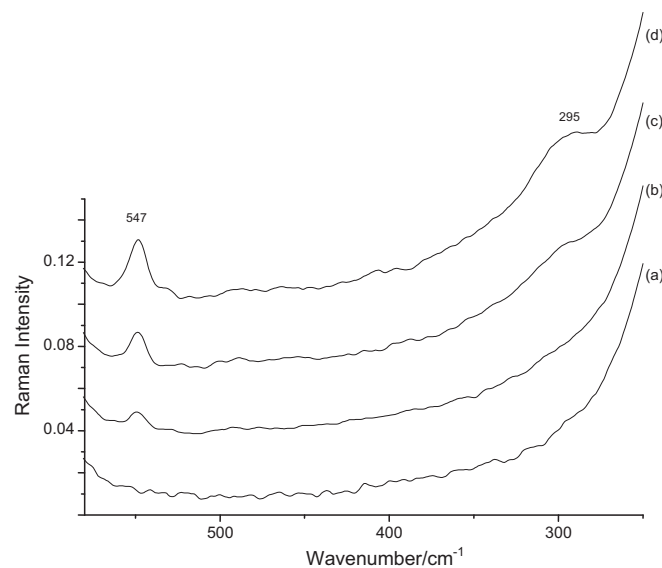
experiments were carried out on a Bruker FT-Raman MultiRAM using the 1064 nm line of the Nd:YAG laser at 500 mW of power and a Ge detector operating at liquid nitrogen temperature. The solutions were inserted in cuvettes containing mirror on one side in order to maximize the signal achieving the detector. Spectra were obtained with 2 cm<sup>-1</sup> resolution at a temperature range from 25 to 150 °C. The same curve-fitting analysis described in our recent papers was here used [3–5].

### 3. Results and discussion

Fig. 1 shows Raman spectra of FA and its solutions with different concentrations of AlCl<sub>3</sub>. The region between 1500 and 1800 cm<sup>-1</sup> (Fig. 1(a)) is characterized by the presence of bands at 1595 ( $\delta_{\text{HNH}}$ ), 1680 and 1703 cm<sup>-1</sup> ( $\nu_{\text{CO}}$ ), where these two latter are due to H-bonded FA molecules in different environments [11,12]. The addition of the salt leads to the appearance of a very well resolved band at 1745 cm<sup>-1</sup> and its intensity is enhanced with increasing salt concentration and at the expense of  $\nu_{\text{CO}}$  (Figs. 1(b)–(d)). It has been therefore attributed to the  $\nu_{\text{CO}}$  vibration of FA complexed to Al(III) and one can note that the observed upshift is larger than those reported for Li(I) and Ca(II), whose the bands are seen at 1714 and 1719 cm<sup>-1</sup>, respectively. In fact, this is an expected result since Al(III) is capable of strongly polarizing the carbonyl group of FA and significantly changing the force constant of this oscillator. Additional information about the most probable FA hybrid may be obtained in the 1200–1500 cm<sup>-1</sup> range. As can be observed, the quite symmetric profile of the 1309 cm<sup>-1</sup> band ( $\nu_{\text{CN}}$ ) is remained and its position is poorly upshifted (3 cm<sup>-1</sup>) by the increase of the salt concentration. Besides it, the selected region also shows bands



**Fig. 1.** Raman spectra of FA and solutions containing different molal concentrations of aluminum chloride at the region characteristic of the solvent: (a) pure FA; (b) 0.3; (c) 0.7; (d) 1.2.



**Fig. 2.** Raman spectra of FA and solutions containing different molal concentrations of aluminum chloride at the region characteristic of the metal-ligand vibrations: (a) pure FA; (b) 0.3; (c) 0.7; (d) 1.2.

at 1391 and 1361 cm<sup>-1</sup>, which correspond to the  $\delta_{\text{CH}}$  modes of non-coordinated and coordinated FA, respectively. The latter arises due to the mixture of the  $\delta_{\text{CH}}$  and  $\nu_{\text{CO}}$  modes [13]. Again, the highest charge density of Al(III) causes a downshift greater (30 cm<sup>-1</sup>) than that observed for Ni(II) and Zn(II), which is equal to 12 cm<sup>-1</sup>. It is important to mention here that the  $\delta_{\text{CH}}$  mode cannot be used to distinguish the resonance FA structures since the downshifts occur for two hybrids. By combining then the spectral changes observed at the  $\nu_{\text{CO}}$  and  $\nu_{\text{CN}}$  regions we can realize that the –CONH– hybrid (II) is present at the investigated solutions. One can also observe in the 900–1200 cm<sup>-1</sup> region that the components originally observed at 1093 (rocking –  $r_{\text{HNH}}$ ) and 1056 cm<sup>-1</sup> (out of plane deformation –  $\pi_{\text{CH}}$ ) are now accompanied by a new feature at 1135 cm<sup>-1</sup> at highest salt concentrations. We believe that it may be assigned to FA complexed to Al(III) because there is also contribution of the  $\nu_{\text{CO}}$  vibration in this band envelope [13]. Furthermore, this region did not show any relevant information as Li(I), Zn(II), Ni(II), Mg(II) and Ca(II) were studied and this one more time confirms the polarizing power of Al(III).

Since the –CONH– hybrid (II) is stabilized by Al(III), the next step is to investigate the low wavenumber region and determine which FA site is directly involved in the coordination process to the metal. Fig. 2 shows the appearance of two bands at 547 and 295 cm<sup>-1</sup> as the salt concentration is increased. The former is often assigned to the Al–O vibration [14,15] whereas the second corresponds to the Al–N mode [8,9]. Hence, both O and N atoms of FA coordinate to the metal and such evidence should be now discussed and compared to our recent works as well as those published by other authors. Maslak et al. [16] reported that coordination through the N atom of an amide would result in deconjugation of the carbonyl group and lead to an increase in its wavenumber value. The stabilization of a structure such as the –CONH– hybrid (II) would be therefore achieved and as can be seen it is in line with our present conclusion. However, the 547 cm<sup>-1</sup> band clearly reveals that the O atom is bonded to Al(III) and thus coordination *via* both O and N sites could be an explanation to the spectral changes observed at the  $\nu_{\text{CO}}$  and  $\nu_{\text{CN}}$  modes, and at low wavenumbers. Indeed, such an interpretation has been documented in some of our papers [1,2,5], but it would be advisable, at this point, to perform us a quantitative analysis in order to determine the average number of FA molecules around Al(III).

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