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RESEARCH PAPER

Preparation and Characterization of Neodymium(III) arginine complex.

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A B S T R A C T:
A new complex of neodymium(III) arginine was prepared from $Nd(NO_3)_3.6H_2O$ and arginine. The preparation involves mixing the metal-ligand by the ratio 1:2 dissolving both in H_2O and then purifying by ethanol/diethyl ether. The primary analyses showed that the mole ratio of the metal−ligand complex is 1:1. The ^{1}H-NMR spectrum of the complex observed a broadness attributed to the coordination of the paramagnetic metal with the ligand. In addition to, the comparison of vibrational spectra of free and coordinated arginine in the region of carbonyl, imine, and amino groups all indicated the occurrence of the complex. The Uv-vis spectra were also inspected where a new band appeared in the range of 240–270 nm assigned to the ligand metal charge transfer.

KEY WORDS: lanthanide; neodymium; arginine; complex
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1. INTRODUCTION:

Arginine has three functional groups (carboxyl, amine, and imine) each one can donate electrons to form hydrogen bonding or to metals having empty orbitals as shown in figure 1.

Arginine exists in the structure of many enzymes. Arginine in one subunit has the ability of binding with another one and with substrates through hydrogen bonding (Wang et al. 2004; and Karsten and Cook 1993). In erythrocytes glycolysis pathway the enzyme bisphosphoglycerate mutase converts 1,3-biphosphoglycerate (1,3-BPG) to 2,3-biphosphoglycerate (2,3-BPG). This substrate 1,3-BPG binds with the enzyme at different amino acids in which arginine is one of them specially at the guanidinium site studied by (Garel et al. 1993), also quoted that "mutation in arginine89 resulted in significant perturbation in the enzyme's catalytic activity". A study made by Fairlie et al. (1997) on arginine complexes, the X-ray and NMR spectra showed that the guanidine group of arginine had contributed in the coordination with Co(III) and Pt (II) ions.

The spectroscopic studies are quit helpful for interpreting the occurrence of the complex (Aiyelabola et al. 2012; and Martins et.al 2003). The arginine infrared spectrum shows bands of C=O stretching in the regions 1700 to 1660 cm^{-1} and N–H deformation from 1650 to 1610 cm^{-1} (Kumar and Rai 2010; Muley et al. 2009; and Wang et al. 2014).

Some of previous investigations of arginine complexes focused on bands shifting of carbonyl stretching around 1700cm^{-1} and of imine stretching around 1550cm^{-1} (Kong and Yu 2007; Ozturk et al. 2014; Wu et al. 2010; and Sunatkari et al. 2015) due to their interactions with metals.

Furthermore, shifting in N–H deformation band around 1630cm^{-1} of the arginine is another indicator taken for assessing the occurrence of the

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complex (Kong and Yu 2007; and Aruna 2007). Therefore, an arginine molecule that contains six donating sites can very likely create a coordination bond with neodymium(III) ion from more than one site. The scope of this study is the synthesis of Nd(III)arginine complex investigating it by techniques of elemental analyses, ^{1}H–NMR, infrared, and Uv-visible spectroscopies to observe any significant changes that may occur.

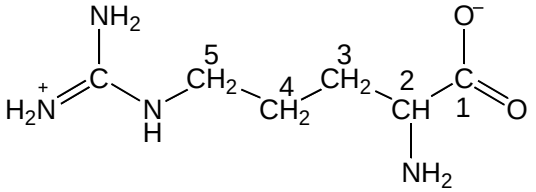

Figure 1. the zwitterion structure of arginine

2. MATERIALS AND METHODS

2.1 Complex Preparation

L-Arginine monohydrate was purchased from Scharlau supplier and neodymium(III) nitrate hexahydrate from Santa Cruz Biotechnology. The synthesis of Nd(III) arginine complex is as the followings; 1mmole $Nd(NO_3)_3.6H_2O$ was dissolved in 10mL H_2O and mixed with 2mmole of arginine also dissolved in 10mL H_2O at temperature 70°C for 2hours. The solution started appearing emulsified, the heating continued until the volume reduced to 10mL. After cooling the solution, 15mL ethanol was added followed by diethyl ether till the complex precipitated. The complex dried at 60°C for one day.

2.2 Analyses

The elemental analysis was performed to estimate the percentage of each element in the free and complexed arginine. The Nd^{3+} ion in the complex was determined through the following steps; first the metal turned into oxides at 550°C for 2 hours, dissolved in 3M HCl, and finally titrated with EDTA at pH 5.5 acetate buffer using murexide indicator (a pilot titration was previously made). Conductivity measurements were performed in DMF solvent purchased from Bruck.

The molar conductivity was experimentally estimated using Friedrich Kohlrausch equation by preparing a series of 10^{-3} molar of the complex at 25°C. The pH of L-arginine solution was also checked at 25°C to see the scale of its protonation using pH-meter Hanna 211. The ^{1}H–NMR spectra were obtained in D_2O solvent by instrument Bruker 500MHz Avance III. The NMR and elemental analyses were accomplished at Department of chemistry/Jordan University/Jordan. The infrared spectra were performed in solid KBr using instrument model Perkin Elmer/ spectrum one FTIR at Department of chemistry/University of Sulaimani. The ultraviolet-visible spectra were obtained by preparing the solutions in distilled water using EMC-LAB UV-6100PC double beam spectrophotometer working at 2nm slit-width.

3. RESULTS

3.1 Elemental analysis

Arginine has four protonation constants. The measured pH is 11.2 so it is expected to be in a zwitterionic form (Fitch et al. 2015) figure 1. The complex synthesis involved mixing 1millimoles of $Nd(NO_3)_3$ with 2millimoles of arginine (Arg) but the results of the elemental analysis showed that the most probable mole ratio of Nd^{3+} arginine matching with the theoretical calculations is 1:1 table 1. The results also showed that one nitrate anion expelled. Therefore, it can be concluded that the Nd^{3+} ion interacted with the ionic oxygen of the carboxylate ion and substituted for the expelled nitrate ion. Hence the chemical formula of the complex becomes $NdArg(NO_3)_2$. The limiting molar conductivity (Λ_o) is 138 $S.cm^2.mol^{-1}$ suggesting 1:2 electrolyte solution (Geary 1971).

$$Nd(NO_3)_3 + Arg \longrightarrow NdArg(NO_3)_2 + NO_3^-$$

Table 1. the elemental analyses of $NdArg(NO_3)_2$ complex.

Elements	Theoretical%	Found%
Nd^{3+}	32.3	30.7
N	19.1	18.1
C	16.4	17.4
H	3	4

3.2 ^{1}H-NMR spectra

The ^{1}H–NMR spectra of zwitterion arginine and its complex were scanned to 20ppm. The free L-arginine shows three peaks; one at 1.55ppm assigned to the hydrogen atoms at C3 and C4 (overlapped) meanwhile the others hydrogen NMR C2 and C5 appear at 3.2 and 3.1 ppm respectively (Wishart et al 2009; and Yanagisawa and Yamamoto 2013) figure 2a.

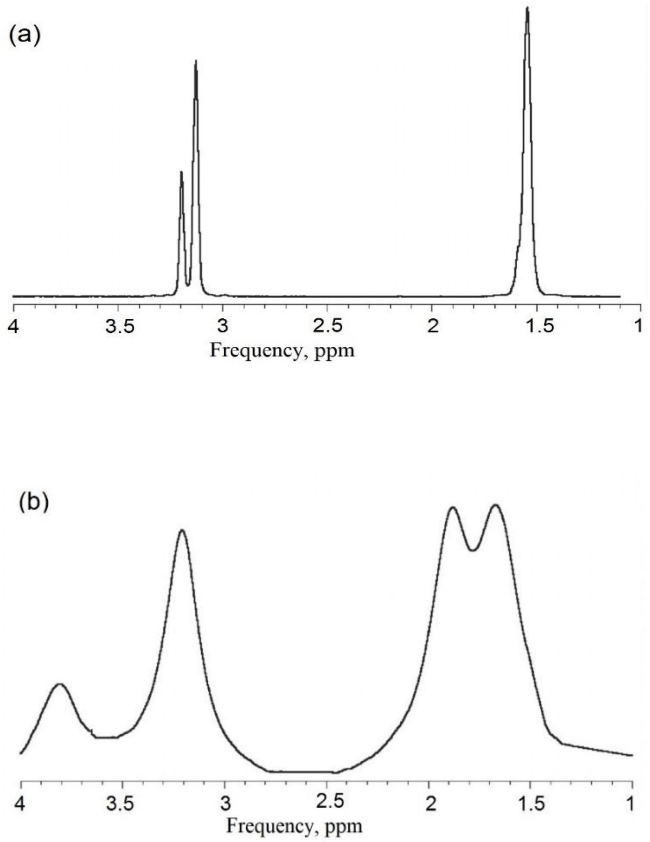

Figure 2. ^{1}H-NMR spectra of (a) Arg and (b) $NdArg(NO_3)_2$ in D_2O

3.3 IR spectra

The IR spectrum of arginine was compared with that of complexed arginine table 2. The high intensity carbonyl stretching band of free arginine that appears at 1679cm^{-1} shifted to 1664cm^{-1} in the spectrum of the arginine complex figure 3.

The stretching band of guanidine-imine group also shows a significant shift but to higher energy from 1555 to 1580 cm^{-1} assigned to the coordination of Nd(III) with imine group (Bush et al. 2008; Forbes et al. 2007; Govani et al. 2009; and Rosu et al. 2005). The broad band 1633–1614 cm^{-1} is expected to be for N–H deformations but does not showed any shift figure 3. In the same time C–NH stretching band at 1138 cm^{-1} shifted to 1115 cm^{-1} after complexation (Govani et al. 2009; Barth 2000; and Petrosyan and Sukiasyan 2008).

Table 2. The infrared spectral data of arginine and its complex

Band		υ / cm^{-1}	
		Arg	$NdArg(NO_3)_2$
	$C{=}O_{str}$	1679	1664
	$C{=}N_{str}$	1555	1582
	$C{-}N_{str}$	1138	1115
NO_3^-	υ_o asym		1384
	υ_1		1500
	υ_3		825

Notes: str stretching; def deformation; asym asymmetric stretching.

Furthermore, the complex IR spectrum shows four bands at 825, 1500 (shoulder), and 1384 cm^{-1} assigned to $\upsilon_3, \upsilon_1, \upsilon_o$ NO_3^- vibrations respectively (Petrosyan and Sukiasyan 2008; Gupta and Sirvastava 2014; Tahaa et al. 2011; and Miller and Wilkins 1952). A band appearing at 1763cm^{-1} assigned to be for the nitrate ion and another one occurred at 551cm^{-1} assigned to Nd–O (Tahaa et al. 2011 and Arif et al. 2001).

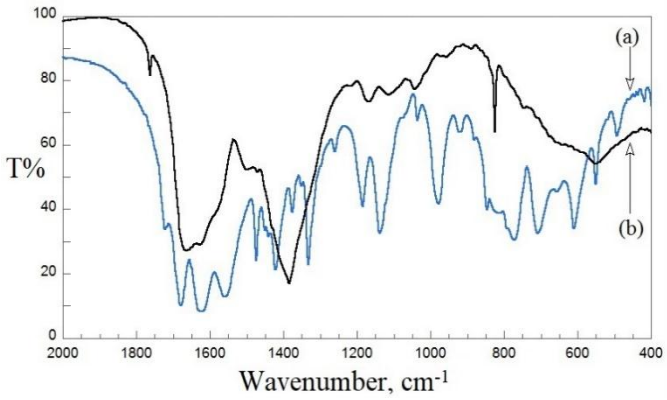

Figure 3. Fourier transform−infrared spectra of (a) L-arginine and (b) $NdArg(NO_3)_2$

3.4 UV–vis spectra

Scanning neodymium nitrate in the Uv-vis region reveals three bands at 348, 302, and 215nm (not shown) figure 4. The complex spectrum shows a new absorption region 240 to 270 nm

neither the free $Nd(NO_3)_3$ ion nor the free arginine showed this band (Otten et al. 2007).

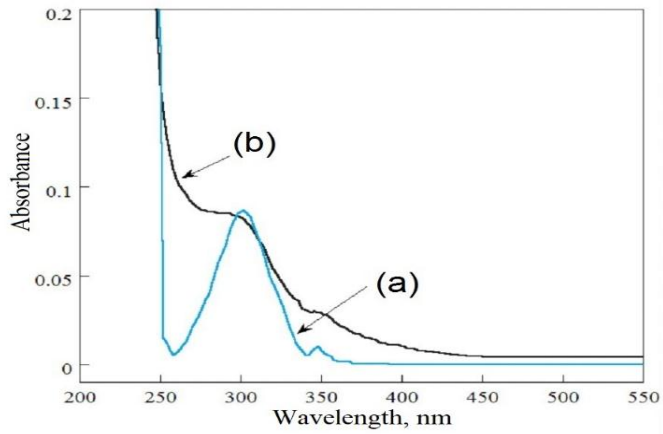

Figure 4. UV-vis spectra of (a) $Nd(NO_3)_3$ and (b) $NdArg(NO_3)_2$ both at $1.88*10^{-3}$ molar in H_2O

4. DISCUSSION

4.1 ^{1}H–NMR

The ^{1}H-NMR spectrum at C2 of the complexed arginine shows a significant broadness and shifting at frequency 3.8ppm which is different from the free arginine (Arg) 3.21ppm figure 2. This broadness and shifting to the low shield field is due to the interaction of paramagnetic Nd(III) with the amino group mostly that is at C2 as quoted by Cotton (2006) "the magnitude of the proton shifts depends upon the distance of the proton from the site of coordination to the lanthanide ion". The complexed arginine spectrum at C3 also shifted from 1.54 to 1.90ppm which shows a greater shift than that of C4 to 1.67ppm.

Overall, these shifting and broadness prove the contribution of amino group at C2 in the coordination bond. It is noteworthy that H-NMR spectrum of arginine could give different frequencies for different optical activities dextro, levo, or mixture also the pH could cause a shift therefore it is recommended to compare the obtained H-NMR with the correct reference which is L-arginine in the current study.

4.2 IR and Uv-vis spectra

This IR shifting of the complexed carbonyl group to low energy resulted from interaction and charge transfer of carboxyl group to the metal ion disrupting the electronic resonance in COO^- letting lesser electronic cloud on the carbonyl group and lower vibrational energy.

As arginine contains three amino groups it is difficult from IR interpretation to conclude which one interacted with the metal ion. Altogether shiftings in energy of COO^-, C=NH, and C–NH bands are interpreted as evidence for their interactions with Nd(III) Barth 2000.

Comparison of the electronic absorption spectra of arginine and its complex resulted in appearance of a new band in 240 – 270 nm assigned to ligand-metal charge transfer, this band was also observed in a previous study on lanthanides by Tahaa et al. (2011).

5. CONCLUSIONS

The analyses revealed that the zwitterion arginine can coordinate with $Nd(NO_3)_3$ through three sites (carboxylate ion, imine, and amino) groups with liberation of one nitrate ion forming $NdArg(NO_3)_2$. The evidences for complex occurrence are based on low energy shifting in IR spectra of carbonyl stretching by $15cm^{-1}$ and high C=N shifting by $27cm^{-1}$ and of the amino groups from 1138 to 1115 cm^{-1}.

Furthermore, the broadness in the H-NMR spectrum for all carbon atoms resulted from surrounding the Nd(III) ion by the carboxylate and guanidine terminuses of the ligand arginine and the amino group at C2 as well. Finally, the polydentate arginine can take the role of a chelating ligand where the Nd(III) encapsulated by the three mentioned groups.

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