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Al(III) complexation by alizarin studied by electronic spectroscopy and quantum chemical calculations

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ABSTRACT

The complexation reaction of Al(III) by alizarin (Az), in methanol solution, has been followed by electronic absorption spectroscopy. Chemometric methods applied to the spectra set have shown the formation of two complexes of stoichiometry 1:1 and 2:1, with stability constants of 6.44 and 11.61, respectively. In the alizarin ligand, the fixation of Al(III) can occur either with the hydroxy-keto site or the catechol site. The comparison between the experimental spectrum of the 1:1 complex and those calculated with time dependent density functional theory, from different hypothetical complex structures, has shown that the first site involved in the Al(III) fixation is the catecholate function. Quantum chemical calculations have also allowed a complete assignment of Az and its 1:1 complex electronic spectra. For both, the observed transitions have essentially a $\pi \rightarrow \pi^*$ character. For the complexed form, only intraligand charge transfers are observed. The chelation of Al(III) engendered some conformational modifications of the ligand, notably at the complexation site level but also at the level of the intermediate ring of Az.

1. Introduction

Discovered a long time ago and extracted from the roots of *Rubia tinctorum* plant, alizarin (1,2-dihydroxy-9,10-anthraquinone), noted Az (Fig. 1), is one of the most known and stable organic pigments, mainly used for colouring textile [1,2]. Nowadays, it is synthesized and studied for applications in many fields as medicine [3,4], solar energy conversion [5,6], metal detection [7]. Complexes formed with metal ions such Ru(III) and Al(III) can be used as UV absorbers [8]. Widely used in painting, it has been studied in the framework of restoring or conserving artworks [9].

Investigations of Az have already been carried out in gas phase [10], solid state [11], and solution in different solvents [12–16], due to the insolubility of hydroxyanthraquinones in several organic solvents. Various techniques allowed the study of Az and its metal complexes: NMR [11], polarography [17], potentiometry [18], Raman [19], absorption and fluorimetric spectrophotometry [20,9]. Quantum chemical calculations have already performed for dihydroxyanthraquinones [21–23] and metal complexes of Az (Cr(III), Ni(II), Cu(II), Zn(II), Cd(II), Fe(III)) [24,7,25]. The Al(III)–Az complex, usually called Turkey Red, belongs to the most used dyes [26], and even if it has already been the subject of some previous works, the complex structure is controversial. Two contradictory hypothesis are proposed in the literature, an Al(III) fixation with the catechol group [27] and a metal chelation with the 1-hydroxy-9-keto group [25].

For metal ion fixation, Az presents two potential sites in competition: the 1,2-dihydroxyl (catechol) and the 1-hydroxy-9-keto groups. If a monodentate fixation mode could be considered, bidentate complexes are usually the most stable ones, for such ligands [28,24]. Thus only chelate complexes have been envisaged in this study. The combination of electronic absorption spectroscopy and quantum chemical calculations is a powerful tool to characterize the structure of complexes in solution but has never been used before to study Al(III) complexation by Az. For reasons of insolubility of Az in water, methanol has been chosen as solvent. The aims of the present work are to: (i) determine the stoichiometries, the stability constants and the pure UV–Vis absorption spectra of Al(III)–Az complexes in methanol, (ii) optimize the molecular geometries by density functional theory (DFT) and calculate electronic transition of Az and its 1:1 complex, (iii) compare the chelating power of the fixation sites in competition and determine the first site involved in the complex formation, (iv) observe the conformational modifications of the ligand engendered by the chelation.

2. Experimental

2.1. Chemicals and preparative methods

Alizarin and sodium chloride (NaCl) were obtained from Acros Organics and used as received without further purification.

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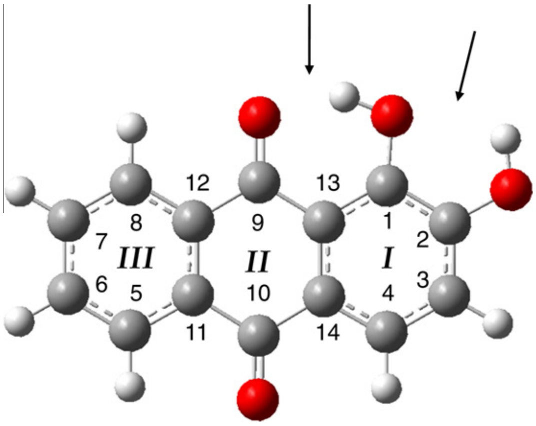

Fig. 1. Chemical structure of alizarin (the arrows indicate the potential fixation sites) with atomic and ring numbering used in the text.

Anhydrous aluminium chloride ($AlCl_3$) was purchased from Fluka Chemika and also used without purification.

To a solution of Az (5×10^{-5} M) in methanol, a solution of $AlCl_3$ (1.25×10^{-3} M) was added dropwise with stirring, under atmospheric conditions at 20 °C, until a final metal/ligand molar ration R ($n_{Al(III)}/,n_{Az}$) of 5:1 was obtained. Methanol solutions were used because of the low solubility of Az in water. Ionic strength was fixed to 0.1 M with NaCl.

2.2. Spectral studies

The UV–Vis spectra were recorded on a CARY 100 (Varian) double-beam spectrophotometer, in the region of 200–800 nm. The use of a flow cell with 1 cm path length has allowed the dosage following when $AlCl_3$ was gradually added in the ligand solution. An apparent pH was also measured during the dosage, with a Hanna pH meter.

2.3. Chemometric methods

The modelling and fitting of data sets obtained from experimental measurements, with the SPECFIT software [29], allowed the determination of the number of absorbing species using a factor analysis procedure (EFA) [30–32] and the estimation of the conditional stability constants (β) of the different complexed forms. Each stability constant corresponds to an equilibrium (1) between Al(III) and the ligand (Az) and expressed by (2):

$$x\mathrm{Al} + y\mathrm{Az} \leftrightarrows \mathrm{Al}_x\mathrm{Az}_y \qquad (1)$$

$$\beta = \frac{[\mathrm{Al}_x\mathrm{Az}_y]}{[\mathrm{Al}]^x[33]^y} \qquad (2)$$

2.4. Quantum chemical calculations

The DFT calculations were performed with the GAUSSIAN 03 program package [33]. Geometries were optimized without symmetry constraint, and electronic transitions calculated by using the Becke three-parameter-Lee–Yang-Parr B3LYP hybrid exchange–correlation functional [34,35]and the 6-311+G(d,p) basis set. These functional and basis set have already been used previously for quantum calculations concerning Az [24,10,6,23]. Solvent effects (methanol) were taken into account by the SCRF method, *via* the polarizable continuum model (IEF-PCM). Vibrational frequency calculations have been performed to ensure that all the optimized structures of the free and complexed Az correspond to energy minima, by checking the absence of imaginary frequency. The low lying excited states (40) were treated within the adiabatic approximation of time-dependent density functional theory. Electronic transitions were calculated from optimized structures in vacuum, then in methanol. Only transitions whose oscillator strengths >0.05 and molecular orbitals with a contribution >15% are reported in this paper. The calculated absorption energies and intensities were transformed with the GAUSSSUM program into simulated spectra using GAUSSIAN functions assuming a constant bandwidth at the half-height of 4000 cm^{-1}. This value constitutes an average width for an absorption band observed in the UV–Vis range.

3. Results and discussion

3.1. UV–Vis absorption spectra of alizarin and its complexes with Al(III)

The electronic spectrum of free alizarin in methanol (Fig. 2) is mainly characterized by two important absorption bands, the first one at 248 nm with two shoulders at 228 nm and 277 nm, and the second one at 429 nm. The position of the band in the long wavelength range corresponds to that observed by Sasirekha et al. in methanol (430 nm) [36], and Miliani et al. in water–dioxane solvent at pH 2.5 (430 nm) [37]. Important spectral modifications were observed when successive small amounts of $AlCl_3$ are added to the solution. A clear decrease of the apparent pH (of roughly 4 units) is noted, that could be explained by hydroxyl functions deprotonation occurring simultaneously with Al(III) fixation. The band initially located at 248 nm shifts toward higher wavelengths to 255 nm and increases in intensity. The change of the solution color observed (orange to red) is due to the disappearance of the band located at 429 nm and the growth of another one at roughly 490 nm. The red shift observed when Al(III) is added has already been previously noted with other metals [18,38]. No isosbestic point is clearly present in the spectral data sets, meaning that a simple equilibrium is not observed at the beginning of the dosage, but that several complexed forms must coexist rather quickly in solution. For large amounts of Al(III) added ($R \geqslant 4.5$), no spectral change occurs and the last recorded spectrum must correspond to the final complex.

3.2. Stoichiometries, spectra and stability constants of the alizarin complexes

The stoichiometry of the complexed forms was determined by the molar ratio method. When absorbance is plotted versus

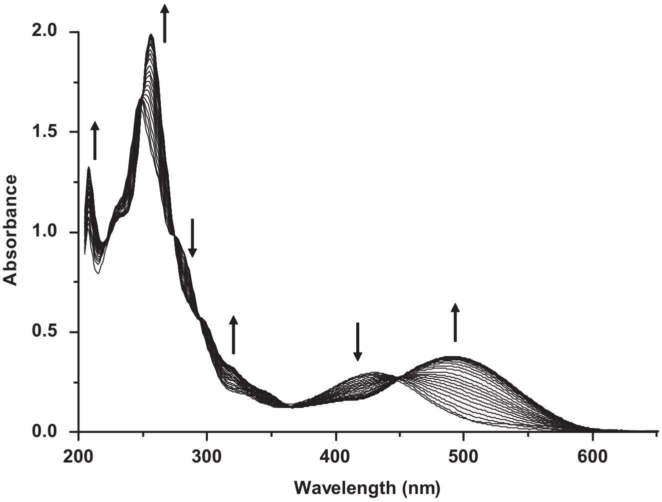

Fig. 2. UV–Vis absorption spectra of alizarin in methanol, in the absence and the presence of $AlCl_3$ for metal/ligand molar ratios varying from 0 to 5.