



Carboxyl groups of citric acid in the process of complex formation with bivalent and trivalent metal ions in biological systems

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ABSTRACT

Binary complexes of citric acid (H_3L – protonated form, H_2L and HL – partly protonated forms, L – fully deprotonated) with d- and f-electron metal ions were investigated. The studies have been performed in aqueous solution using the potentiometric method with computer analysis of the data, electron paramagnetic resonance, infrared, visible as well as luminescence spectroscopies. The overall stability constants of the complexes were determined. Analysis of the equilibrium constants of the reactions and spectroscopic data has allowed determination of the type of coordination and effectiveness of the carboxyl groups in the process of complex formation. On the basis of potentiometric titration for d-electron were found dimeric and monomeric type of complexes and for f-electron four type of complexes: MHL, ML, $ML(OH)$ and $ML(OH)_2$.

1. Introduction

There is no doubt that metal ions play significant role in biological processes as well as human metabolism e.g. for transport of oxygen, functions of enzymes, functioning of the central nervous system. These metal ions in trace amounts are important to sustain life but their accumulation can contribute to some serious diseases (e.g. Huntington's, Alzheimer's, Parkinson, Wilson and Merkes diseases) [1–3]. Moreover complexes of d-electron metal ions such as copper, cobalt or nickel are interesting as model compounds of active sites of biological enzymes [4–9], essential for folate and fatty acid metabolism and are associated with the active part of hydrogenase and are involved in hydrogen oxidation [10–17].

The lanthanide(III) compounds do not naturally occur in living organisms but are useful as a radiopharmaceuticals and magnetic resonance imaging (MRI) contrast agents. In particular, gadolinium complexes are applied as contrasting agents in MRI, one of the most accurate imaging techniques for diagnostic purposes or for monitoring of therapy effects, usually applied for patients with cancers, diseases of heart and central nervous system and other maladies. The wide variety of structural types of rare-earth carboxylates depend on high and variable coordination numbers available to the 4f-block elements and their unique f-f electronic transition [9,18–21]. Moreover the lanthanide(III) complexes show antibacterial and antifungal properties, and the activity of the complexes is higher than that of free ligands [22,23].

On the other hand, the lanthanide(III) compounds can be used as a very effective catalysts with high site selectivity for the hydrolytic cleavage or transesterification of RNA and as a substance promoting DNA cleavage [24]. The unique properties of lanthanide complexes make them applicable as magnetic materials e.g. lanthanide ions have been proven to be particularly suitable for the synthesis of 4f Single Molecule Magnets (SMM) [25–29].

Citric acid belongs to the strongest fruit acid and is commonly found in human organisms and plays a crucial role in the Krebs cycle also called the citric acid cycle. It is an essential compound in a number of metalloenzyme active sites such as aconitase iron-sulfur cluster and nitrogen fixation homocitrate synthase ($NifV^-$). Salts of citric acid occur in bones where they are responsible for the regulation of size of apatite crystals. Citric acid molecule comprises one α -position hydroxyl group, one α -position carboxyl group and two β -position carboxyl groups, and contains at least seven potential donor sites capable of coordinating metal ions. This type of structure permits formation of coordination complexes of novel structure types [30–34].

Citric acid with the seven potentially O-donor atoms is an asymmetric ligand which can be assembled around metal ions in diverse arrangements as a chelating and bridging spacer. These properties permit formation of coordination complexes of novel structure types. Therefore citric acid is a very attractive agent in design of potentially useful compound as a monomeric, binuclear and polymeric complexes with both d- and f-electron metal ions [35–39].

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Table 1
Protonation constants of citric acid (standard deviation are given in parenthesis).

Species	Overall protonation constants (log β)		Reactions	Successive protonation constants (logK _e)
H ₃ Cit	12.67 (3)	12.67 [50]; 12.71 [51]	H ₂ Cit ⁻ + H ⁺ ⇌ H ₃ Cit	3.04
H ₂ Cit	9.63 (2)	9.78 [50]; 9.84 [51]	HCit ²⁻ + H ⁺ ⇌ H ₂ Cit ⁻	4.24
HCit	5.29 (2)	5.53 [50]; 5.57 [51]	Cit ³⁻ + H ⁺ ⇌ HCit ²⁻	5.39

Compounds based on d- and f-electron metal carboxylate complexes are of interest because of their relevance in a wide range of applications in materials science, including superconductors, catalysis, and luminescence probes as well as in the process well known as the “antenna effect” [40].

This paper presents results of the equilibrium and spectroscopic studies of the metal ions/citric acid systems and effectiveness of the carboxyl groups of citric acid in coordination was described.

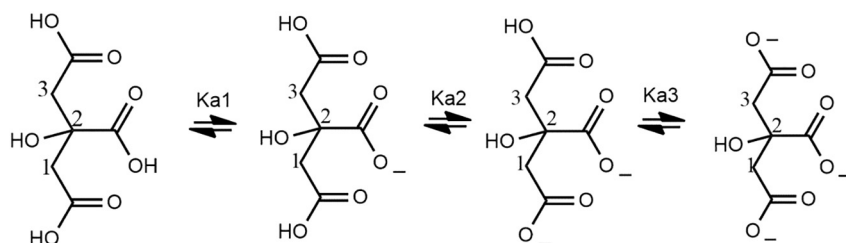
2. Materials and methods

2.1. Materials

Citric acid (Cit) was purchased from Sigma and was used without further purification. Copper(II), nickel(II) as well as cobalt(II) nitrate from Merck, were purified by recrystallization from water. Lanthanum(III), neodymium(III), europium(III), gadolinium(III), terbium(III), holmium(III) and lutetium(III) nitrates(V) and chlorides were obtained from Aldrich and were used without further purification. The concentrations of metal ions were determined by the method of Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES). All solutions and experiments were prepared using demineralized carbonate-free water (conductivity 0.055 μ S).

2.2. Equilibrium study

Potentiometric titrations were carried out using Titrand 905 Metrohm equipped with an autoburette with an i-electrode Metrohm 6.0280.300 calibrated in terms of hydrogen ions concentration prior to each titration [41–46]. Before each series of measurements, the pH-meter indication was corrected with the use of two standard buffer solutions of pH 4.00 and pH 9.22 at 20 \pm 1 °C. Potentiometric titrations were carried out for the metal:ligand ratios of 1:1, 1:2 and 2:1 (the concentration of citric acid in all systems was 0.001 M). All potentiometric titrations were performed in the atmosphere of neutral gas (helium - Ultra High Purity), at the constant ionic strength of 0.1 M (KNO₃), temperature 20 \pm 1 °C, in the pH range from 2.5 to 10.5, using as a titrant CO₂-free NaOH at a concentration of 0.1885 M. In all systems in the whole pH range, no formation of precipitate was observed. Eight or more titrations were performed for each particular system and 150–350 points from each titration curve were used for computer analyses. The protonation constants of the ligands and stability constants of the complexes were determined using the

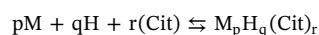


HYPERQUAD program [41,43–45]. The computer program uses the non-linear method of least squares to minimize the sum (S) of the squares of residuals between the observed quantities (f_i^{obs}) and those calculated on the basis of the model (f_i^{calc})

$$S = \sum_{i=1}^n w_i (f_i^{obs} - f_i^{calc})^2$$

n – number of measurements, w_i – statistical weight.

The iteration procedure allows determination of the types (stoichiometry) and thermodynamically stability of the complexes formed in the systems studied. The testing began with the simplest hypothesis and then the models were expanded to include progressively more species, and the results were scrutinized to eliminate the species rejected by the refinement processes. The stability constants were evaluated for the equilibria:



where M = metal ion (charges were omitted for simplicity)

and calculated in the following equation:

$$\log\beta = [M_pH_qCit_r]/[M]^p[H]^q[\text{Cit}]^r$$

Hydrolysis constants of metal ions were taken into account in the computer analysis of potentiometric data. The pK_w value determined was 13.89. The correctness of the model was confirmed by verification of the results obtained [47–49]. The distribution diagrams of particular systems were obtained by the HySS (Hyperquad Simulation and Speciation) program [41].

2.3. Visible (Vis) spectroscopy

Samples for visible spectroscopy (d-d transitions, f-f and f-d lanthanide transitions) studies were prepared in water at the metal:ligand ratio 1:1 and the metal ions concentration of 0.05 M. The spectra were recorded at room temperature on Evolution 300 UV–VIS spectrometer made by ThermoFisher Scientific (resolution 0.2 nm) using quartz cell with 1 cm path length and on Shimadzu UV-2401PC (resolution 0.05 nm) for characterizing the system Nd(III)/Cit.

2.4. EPR spectroscopy

Samples for EPR studies were prepared in a water:glycol mixture (3:1 v:v) at the metal:ligand molar ratio and concentration of the metal ions 0.005 M. The spectra were recorded at –196 °C, using glass capillary tubes (volume 130 μ m³) and on an SE/X 2547 Radiopan spectrometer.

2.5. IR spectroscopy

IR spectra measurements were performed by dissolving the relevant species (citric acid and metal ions) in D₂O and adjusting pH by addition of NaOD or DCl. The pH values were corrected according to the formula pD = pH meter readings + 0.4 [46]. The metal concentration for the IR studies was 0.25 M and the metal:ligand ratio was 1:1. IR spectra were recorded on an ISS 66 v/S Bruker spectrometer (resolution of 2 cm⁻¹), in the cells with Si windows (thickness 100 μ m).

Fig. 1. Scheme of citric acid dissociation.

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