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Two novel Cr(III) complexes $[Cr(SA)_2(en)]TBA$ and $[Cr(SA)(en)_2]Br$: Synthesis, characterization and spectral studies

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ABSTRACT

In this paper, two types of salicylate Cr(III) complexes $[Cr(SA)_2(en)]TBA\cdot H_2O$ (**I**) and $[Cr(SA)(en)_2]Br\cdot H_2O$ (**II**) have been synthesized (TBA = Tetrabutylammonium, SA = salicylate, en = ethylenediamine) and determined by X-ray crystallography. Then competition reaction with ethylenediamine-N,N,N′,N′-tetraacetic acid (EDTA) or apoovotransferrin (apoOTf) was monitored by UV–Visible and fluorescence spectra at 37 °C. It indicated that decomposition rate of $k_{(I)}$ is smaller than $k_{(II)}$. In the reaction with apoOTf, the releasing salicylate ligands will further be combined to OTf along with the serious fluorescence quenching of salicylate.

Chromium(III), an important part of glucose tolerance, is a necessary microelement, playing an important role in normal physiological function of human bodies [1–5]. Till now, many Cr(III) complexes have been synthesized and fully studied, such as $Cr(pic)_3$ [6], $[Cr(D\text{-}Phe)_3]$ [7], NBC [8], CDNC [9], LMWCr [10] and Cr(Amino acid) [11]. Although so many Cr(III) complexes have been used in dietary, most are inadequate or poorly characterized. Furthermore, bioavailability and biological activity of these Cr(III) compounds are different due to the ligand to which Cr(III) is bounded [12]. Therefore there still remains a need in the art for an improved synthetic Cr(III) compound, which demonstrates improved biological activity, bioavailability, stability, solubility and/or sensory characteristics [13]. On the other hand, there is some controversy surrounding the exact biochemical forms of Cr(III) in biological systems, such as intracellular mechanisms [4], extracellular model [14], redox mechanisms [15] and iron homeostasis model [16]. The topic has been the subject of many experimental reports and continues to be investigated.

It should be noted that salicylic acid (H_2SA) can reduce the symptoms related to type II diabetes [17]. Salicylic acid and Cr(III) are hoped to have synergistic effects in diabetes. Many salicylate Cr(III) complexes such as $[Cr(SA)(en)_2]^+$ were composed before by our team [18–20]. In this paper a new type of complex, $[Cr(SA)_2(en)]^-$, is composed, and the reaction with apoovotransferrin (OTf) is studied. The kinetics difference is supposed to affect the biological activity.

The reactions of $CrCl_3\cdot 6H_2O$ (5 mmol), salicylic acid (10 mmol), ethylenediamine (en, 3 ml) and Tetrabutylammonium (TBA^+) in methanol led to the formation of $[Cr(SA)_2(en)]TBA\cdot H_2O$ (**I**). The of $CrCl_3\cdot 6H_2O$ (2.5 mmol), salicylic acid (2.5 mmol), KBr (2.5 mmol) and en in methanol led to the formation of $[Cr(SA)_2(en)]Br\cdot H_2O$ (**II**) [21]. X-ray quality single crystals were formed by slow evaporation of the solutions at room temperature.

According to single crystal X-ray analysis [22], complex (**I**) is composed by $[Cr(SA)_2(en)]^-$ anion and TBA^+ cation (Scheme 1). Cr(III) atom is six-coordinated in octahedral coordination geometry by two phenolic hydroxyl oxygen, two carboxylate oxygen from two salicylate and two nitrogen atoms from one ethylenediamine molecule, respectively. Unfortunately, one of the salicylate plans is disordered. Bond lengths and angles in the anions are within the range absorbed in other studies. The average bond length is Cr–N = 2.089, and Cr–O = 1.953 Å. The sole en ring adopts the configuration δ. The maxima d → d transition ($^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$) appear at 540 nm. Complex (**II**) consists of the $[Cr(SA)(en)_2]^+$ cation and Br^- anions. Cr(III) atom is six-coordinated by one phenolic hydroxyl oxygen, one carboxylate oxygen from the salicylate and four nitrogen atoms from two ethylenediamine molecules, respectively. The average bond length is Cr–N = 2.104, and Cr–O = 1.940 Å. These two en rings adopt the configuration $\lambda\delta$, respectively. In contrast to complex (**I**), the maxima d → d transition ($^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$) peak occur at 510 nm in complex (**II**).

Chromium(III) because of its d^3 electronic configuration forms stable and kinetically substitutional inert complexes, which is usually required for many days for the kinetics studies [23]. In order to research the interaction of the complex with transferrin, EDTA was employed as a simple competitive ligand first. To examine the transfer of Cr(III) from complexes to EDTA, 9 equiv. of EDTA was added to 31 μM complexes in 0.01 M Tris–HCl, pH 7.4. The reaction mixture is stored at 37 °C. Both the UV–vis spectra and fluorescence spectra

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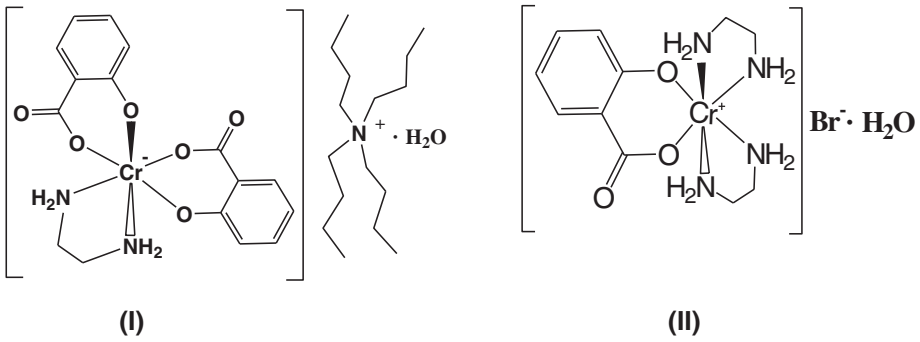

Scheme 1. Structure of $[Cr(SA)_2(en)]^-$ (**I**) and $[Cr(SA)(en)_2]^+$ (**II**).

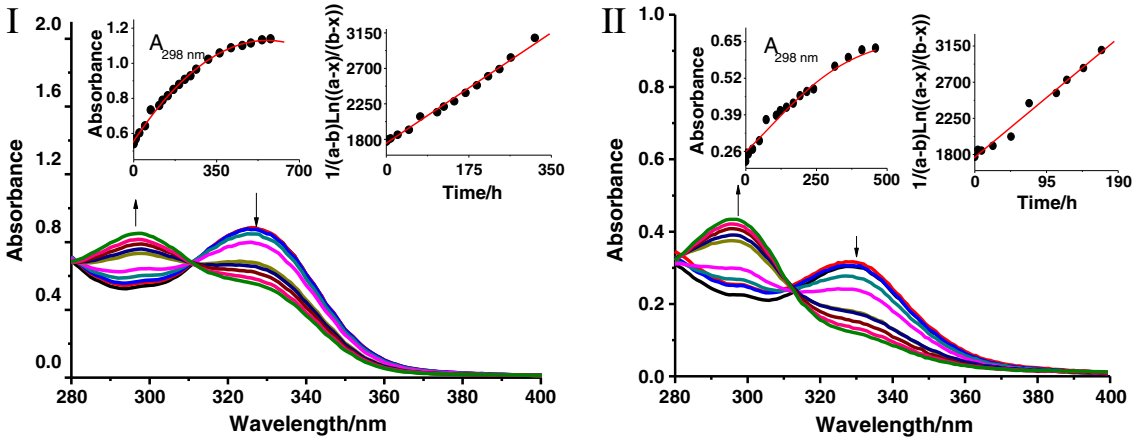

Fig. 1. The changes of absorption spectra at different time for the mixture of 0.15 mM complexes (**I**) or (**II**) with 9 equiv. of EDTA, inset: curves of absorbance at 298 nm with time (fitted by $\ln[(a-x)/(b-x)]=(a-b)(kt+c)$) and plot of $1/(a-b)\ln((a-x)/(b-x))$ vs. time, a = 0.15 mM, b = 1.4 mM, $x=a(A_0-A_t)/(A_0-A_\infty)$.

were monitored as a function of time until the spectra became constant with time. The UV–vis spectra and fluorescence spectra are shown in Figs. 1 and 2.

The second rate constants were obtained, which were shown in Table 1, respectively. The rate constants from the UV–vis spectra and fluorescence spectra are in good agreement. It reveals that the Cr(III) complex is destructed completely in the competition of EDTA and free R-SA^{2-} ligand is gradually released from the Cr(III) ion [18]. Furthermore, the rate constant k_{EDTA}(**II**) = 2.3×10^{-3} $M^{-1}S^{-1}$ is bigger than k_{EDTA}(**I**) = 1.2×10^{-3} $M^{-1}S^{-1}$, indicating that complex (**I**) is stable than complex (**II**). The stability is connected with various factors. First, it is due to the different Cr–N bond lengths in these two complexes. We find that the average Cr–N bond length in complex (**I**) is about 2.089 Å, which is a little shorter than that of Cr–N in complex (**II**) (about 2.104 Å). Second, sterically hindered salicylate rings will hold back the attack of EDTA, the more rings the Cr(III) complex has, the more steric hindrance it has. Obviously bigger steric hindrance at the reactive Cr(III) center in complex (**I**) would impede the substitution of en ligand. Third, the electrostatic interactions of the negatively charged ions of $EDTA^{4-}$ and $[Cr(SA)_2(en)]^-$ (**I**) tend

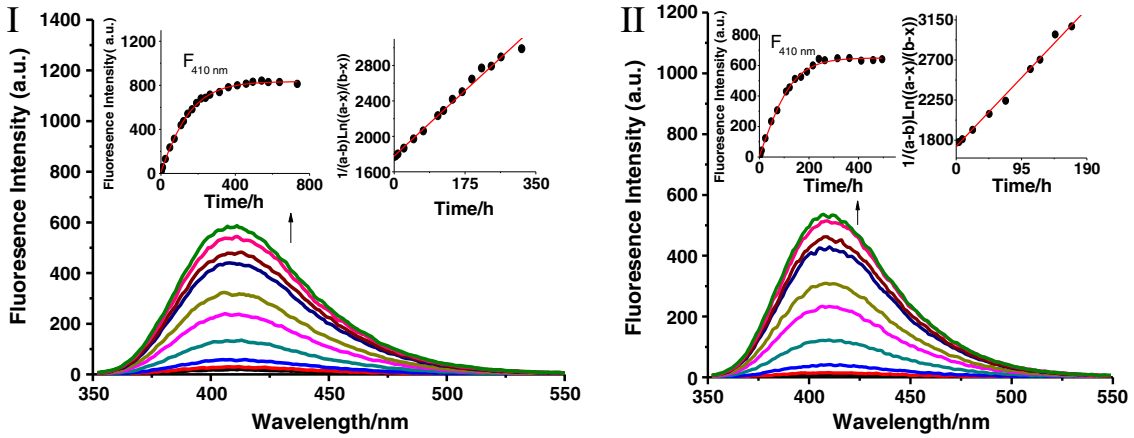

Fig. 2. The changes of fluorescence spectra at different time for the mixture of 0.15 mM complex (**I**) or (**II**) with 9 equiv. of EDTA, inset: curves of fluorescence intensity at 410 nm with time (fitted by $\ln[(a-x)/(b-x)]=(a-b)(kt+c)$) and plot of $1/(a-b)\ln((a-x)/(b-x))$ vs. time, a = 0.15 mM, b = 1.4 mM, $x=a(F_0-F_t)/(F_0-F_\infty)$.