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Aspartic acid interaction with cobalt(II) in dilute aqueous solution: A ^{57}Co emission Mössbauer spectroscopic study

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Abstract Emission (^{57}Co) Mössbauer spectra of the aspartic acid—$^{57}CoCl_2$ system were measured at $T = 80$ K in frozen aqueous solution and in the form of a dried residue of this solution. The Mössbauer spectra, besides a weak contribution from after-effects, showed two Fe^{2+}/Co^{2+} components which were ascribed to octahedrally and tetrahedrally coordinated $^{57}Co^{II}$ microenvironments in the Asp–cobalt(II) complex. This dual coordination mode may be due to the involvement of the second terminal carboxylic group of aspartic acid in the coordination sphere of Co.

Keywords Cobalt(II) complexes · Aspartic acid · ^{57}Co emission Mössbauer spectroscopy

Abbreviations

EMS Emission Mössbauer spectroscopy
Asp Aspartic acid

1 Introduction

Interaction of amino acids and oligopeptides with transition metal ions is of general interest as an approach to modelling metal binding within the active centres of

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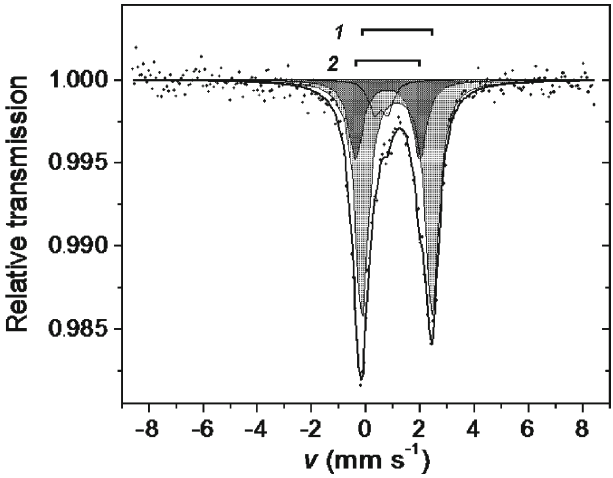

Fig. 1 Emission Mössbauer spectrum of aspartic acid (0.2 ml, 2 mM) incubated with 1.2 mCi $^{57}CoCl_2$ and then rapidly frozen in liquid nitrogen (dried solution; measured at $T = 80$ K). The positions of the two main doublets (1 and 2; shaded areas) corresponding to daughter $^{57}Fe^{II}$ forms (see Table 1, sample "Dried residue") are shown above the spectrum (the third weaker narrow doublet corresponds to daughter $^{57}Fe^{III}$ resulting from after-effects of the 57Co→^{57}Fe transition)

metalloenzymes, where usually a few amino acid residues form a specific cation-binding site [1, 2]. As for ^{57}Co emission Mössbauer spectroscopy (EMS), which has so far been rarely used in biological research [3–5], such studies are also necessary to form a database for a reliable interpretation of EMS data obtained for more complicated biological systems [4–6].

Aspartic acid (Asp; HOOC–CH(NH_2)–CH_2–COOH), an amino acid commonly present as a constituent in proteins [7], is also found, among other free amino acids, in plant root exudates [8]. K-Mg aspartate is a well-known medicine widely used in adjuvant therapy of heart diseases [9]. In addition, transition metal aspartates are used as a bioavailable form of mineral additives in feedstuff [10].

In this work, interaction of L-Asp with cobalt(II) ions in aqueous medium was studied using ^{57}Co EMS in frozen solution and for its dried residue.

2 Experimental

Emission Mössbauer spectra of the aspartic acid—$^{57}CoCl_2$ system (0.2 ml, 2 mM Asp, incubated with 4.5 MBq carrier-free $^{57}CoCl_2$ and then rapidly frozen in liquid nitrogen) were measured at $T = 80$ K in frozen aqueous solution. The air-dried residue of this solution was also measured at 80 K. Details of the measurement procedure were reported earlier [6]. The Mössbauer spectra were evaluated using the MOSSWINN program [11].

3 Results and discussion

A typical emission spectrum is shown in Fig. 1; the calculated Mössbauer parameters are listed in Table 1. For both the spectrum of the frozen aqueous solution and that of its dried residue, the best fit was achieved using three components, with two quadrupole doublets representing different high-spin daughter ferrous forms stabilised after the ^{57}Co→^{57}Fe nuclear transition (see Table 1). The residual $^{57}Fe^{III}$,

Table 1 Mössbauer parameters calculated from ^{57}Co emission Mössbauer spectra for aspartic acid (0.2 ml, 2 mM) incubated with 1.2 mCi $^{57}CoCl_2$ and then rapidly frozen in liquid nitrogen (measured at $T = 80$ K, in frozen aqueous solution or dried)

Sample	Multiplet[a]	δ,[b] mm s^{-1}	Δ,[c] mm s^{-1}	Γ_{exp},[d] mm s^{-1}	A,[e] %
Frozen solution	Doublet 1	1.21(2)	2.82(3)	0.60(3)	72(7)
	Doublet 2	0.96(7)	2.3(1)	0.7(1)	19(8)
Dried residue	Doublet 1	1.15(1)	2.60(1)	0.59(2)	68(5)
	Doublet 2	0.80(3)	2.37(5)	0.63(7)	24(5)

[a]Main doublets corresponding to daughter $^{57}Fe^{II}$ forms stabilised after the $^{57}Co \rightarrow ^{57}Fe$ nuclear transition (the residual $^{57}Fe^{III}$ forms result from after-effects). [b]Isomer shift (relative to α-Fe at room temperature). [c]Quadrupole splitting. [d]Full line width at half maximum. [e]Relative resonant absorption area. Calculated errors (in the last digits) are given in brackets.

which accounts for less than 10% of the spectral area in each spectrum, is due to after-effects [3, 5, 6]. Note that the resulting species under study using EMS may be described as an ^{57}Fe complex substituted for the 'parent' ^{57}Co binding site (retaining its geometry) [6]. In ^{57}Co emission Mössbauer spectra, lines are commonly broader than those in ^{57}Fe absorption experiments owing to special effects [5, 6, 12]. Thus the Γ_{exp} values obtained (see Table 1) are quite reasonable.

It should be noted that our earlier EMS data for other two amino acids, *o*-aminobenzoic (anthranilic) acid and tryptophan, showed one daughter $^{57}Fe^{II}$ component only in each case [6]. In the case of Asp, the presence of the second terminal carboxylic group (in addition to the typical carboxylic group with the neighbouring α-amino group) allows a dual coordination mode. Note that in the system studied, the Asp concentration (2 mM) was by ca. two orders of magnitude higher than that of $^{57}Co^{2+}$, allowing an equilibrium between the two complex forms in solution.

Thus, the parameters of doublet 1 (see Table 1) are typical for an octahedral coordination microenvironment of the parent high-spin $^{57}Co^{II}$ "inherited" by the daughter $^{57}Fe^{II}$. The significantly lower δ and Δ values for doublet 2 in both cases evidently represent tetrahedral coordination, which is relatively common for cobalt(II) complexes [1, 6].

4 Conclusions

^{57}Co emission Mössbauer spectra of the aqueous aspartic acid—$^{57}CoCl_2$ solution (both in frozen state and in dried form at $T = 80$ K) revealed two Co^{2+} components which can be ascribed to octahedral and tetrahedral $^{57}Co^{II}$ coordination in the Co^{II}-aspartic acid complex. This dual coordination mode can be interpreted as being due to the partial involvement of the additional terminal carboxylic group of aspartic acid in the coordination sphere of Co^{II}.

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