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Mössbauer and FTIR spectroscopic studies of iron anthranilates: coordination, structure and some ecological aspects of iron complexation

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Abstract

The data on the coordination and structure of iron(II) and iron(III) anthranilates in the solid state and in aqueous medium are presented and discussed, as studied using Mössbauer (for solid products and frozen solutions) and FTIR spectroscopy (for solid samples). Whereas, in slightly acidic nitrate solutions under aerobic conditions ferric ions can still be gradually reduced by anthranilic (o-aminobenzoic) acid, which may have some ecological significance, in circumneutral media this process is retarded. Mössbauer parameters calculated for iron(II) and iron(III) anthranilates, as well as characteristic vibration modes of certain functional groups involved in coordination with iron cations are discussed. The FTIR data obtained for ferrous anthranilates, as compared to anthranilic acid, definitely exhibit the direct involvement of both the carboxylic and the amino groups of anthranilic acid in coordination with iron. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Iron, as one of the generally most essential microelements [1], and anthranilic (o-aminobenzoic) acid (AA) are both well known to be of significant biological value. AA, being a metabolic product in some bacteria [2,3], is also involved in the biosynthesis of phytohormones (auxins) and their precursors [4,5]. Iron is essential for some enzymatically catalysed

reactions involving AA [6,7], while the latter may under certain conditions act as a microbially excreted iron(III)-solubilizing agent under iron deficiency [8] instead of siderophores commonly used by many soil microorganisms [1] (but via a mechanism different from that of siderophores [9–11]). Iron anthranilates are also of value for technology (as additives to polymeric materials) [12,13] and in analytical chemistry [14].

Diverse structural aspects of AA molecules in different states, as studied both by semiempirical calculation methods and spectroscopic techniques (including vibrational spectroscopy), have been

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reported (see, e.g. Ref. [15] and references cited therein).

In this article, the data on the coordination and structure of iron(II) and iron(III) anthranilates in the solid state and in aqueous solution are presented and discussed as studied using Mössbauer (for solid products and frozen solutions) and FTIR spectroscopy (for solid samples). These two techniques are complementary in that the former is unique in characterizing the electron density and the degree of the electric field symmetry at the iron nuclei, which are related to the oxidation state and the coordination environment of iron atoms [16,17], whereas the latter features the state of functional groups of the ligands and the overall structure of the molecular species under study.

2. Materials and methods

2.1. Sample preparation

2.1.1. Solid samples

Solid iron(II) anthranilates were precipitated from freshly prepared filtered warm (ca. 50°C) aqueous 0.15 M solutions of ferrous sulphate heptahydrate (reagent grade) by their dropwise addition to solutions of anthranilic acid (Serva) neutralized with 1 M KOH (final anthranilate concentration 0.3 M and pH 6; final iron-to-AA molar ratio 1:2); where appropriate, the pH of the AA solution was adjusted to 8 using KOH solution. The precipitates were separated by decantation and filtration, thoroughly washed several times with bidistilled water and twice with acetone (chemical purity) on the filter and dried in air at ambient temperature.

2.1.2. Iron-containing aqueous solutions

For Mössbauer measurements in aqueous media, iron(III) nitrate solution was prepared by dissolving ^{57}Fe metal (95.6% enriched isotope obtained from the centre for radionuclide diagnostics at the Russian Foundation for basic research, Moscow) in a slight excess of ca. 50% nitric acid (analytical reagent grade) at elevated temperature, partially drying the resulting solution in air at ca. 50°C up to the formation of crystals and further redissolving the latter in doubly distilled water up to the iron(III) concentration of 0.1 M (stock solution). The absence of iron(II) in

the stock solution was confirmed by special Mössbauer measurements. The concentrations of iron(III) and anthranilic acid (Sigma) in the solution under study were adjusted to 0.01 and 0.03 M, respectively (pH ca. 5). After mixing, the solution was allowed to stand at room temperature for a certain period of time and then rapidly frozen by inserting it dropwise into a sample holder cooled with liquid nitrogen.

2.2. Mössbauer spectroscopic measurements and data treatment

Mössbauer spectra of the frozen samples placed in a cryostat filled with liquid nitrogen (at ca. 80 K) were collected using a conventional constant-acceleration Mössbauer spectrometer combined with a computer-operated multichannel analyser; a $^{57}Co[Rh]$ source used was calibrated relative to α-Fe at ambient temperature. Room-temperature measurements of solid samples were performed similarly (in the same cryostat after evaporation of liquid nitrogen, retaining the mounting geometry of the solid sample relative to the gamma-ray beam path, after the sample temperature had reached that in the laboratory). Standard computer statistical analysis included fitting the experimental data obtained to a sum of Lorentzian-shaped component lines using a least squares fit, which enabled calculation of the values of isomer shift (IS; all data are given relative to α-Fe), quadrupole splitting (QS), linewidth (i.e. full width at half maximum, FWHM), as well as partial resonant absorption areas of superimposed components composing the overall spectrum, which represent relative contents of the corresponding iron forms assuming a common recoilless fraction for all forms.

2.3. FTIR spectra acquisition

Solid air-dried samples (mentioned earlier) were carefully pressed into pellets with spectroscopically pure KBr (Merck). Spectra were collected with a total of 60 scans at a resolution of 4 cm^{-1} in the transmission mode (mid-infrared region, 4000–400 cm^{-1}) using a Perkin–Elmer Fourier transform IR spectrometer (Model 2000; UK) coupled with a personal computer loaded with an IR data manager program supplied by the manufacturer. Unless otherwise stated, all measurements were conducted at 295 ± 3 K.
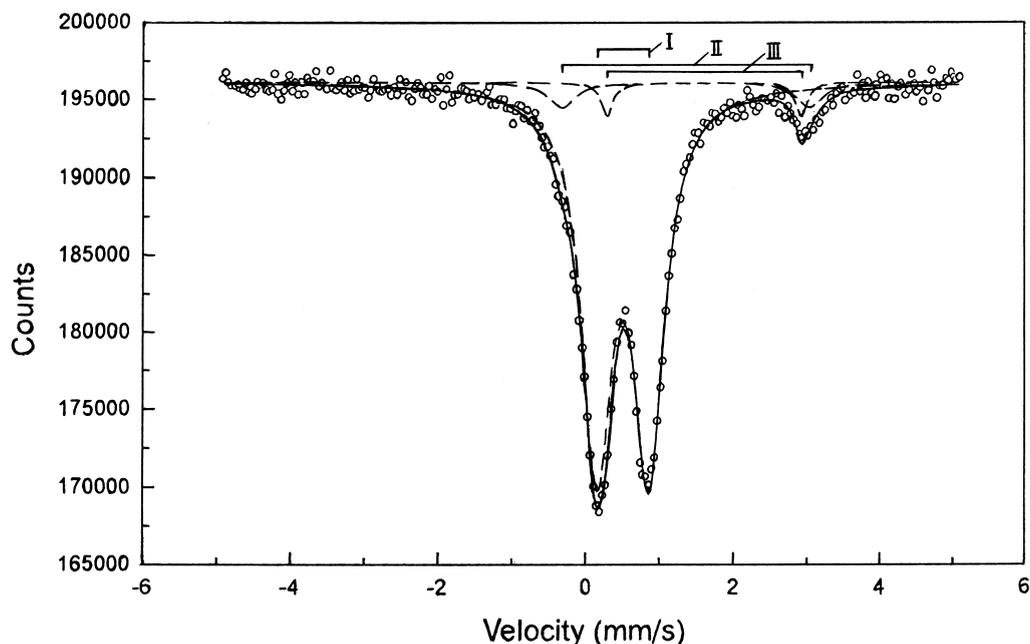
Fig. 1. Mössbauer spectrum of [57]Fe[III] nitrate solution containing anthranilic acid (measured at $T = 80$ K), frozen 10 min after mixing. Subspectra represent calculated Lorentzian-shaped components (I–III see text and Table 1) composing the resulting spectrum (solid line) computer-fitted to the experimental data (points); the same for Fig. 2.

3. Results and discussion

Both iron(II) and iron(III) ions are known to form complexes with the anthranilate ion, which are poorly soluble in aqueous media [14,18]. However, an essential extractability of the ferric complex with oxygen-containing nonaqueous solvents, in contrast to the ferrous anthranilate (and a number of other divalent

Table 1
Mössbauer parameters (see also Figs. 1–3) for [57]Fe-containing anthranilic acid solution ($T = 80$ K) at pH about 5 and dried solid samples of iron(II) anthranilates precipitated at pH 6 and 8

Figure	pH	T,(K)	Spectral component	IS,[a] (mm/s)	QS,[b] (mm/s)	FWHM,[c] (mm/s)	Fe oxidation state	S_r^d, (%)
1	5	80[e]	Doublet I	0.51 ± 0.01	0.71 ± 0.01	0.49 ± 0.02	III	91.5
			Doublet II	1.36 ± 0.03	3.36 ± 0.06	0.42 ± 0.22	II	5.3
			Doublet III	1.61 ± 0.03	2.64 ± 0.06	0.20 ± 0.09	II	3.2
2	6	80	Doublet	1.25 ± 0.01	2.71 ± 0.01	0.40 ± 0.01	II	100
—	6	298	Doublet	1.13 ± 0.01	2.11 ± 0.01	0.43 ± 0.01	II	100
2	8	80	Doublet I	1.25 ± 0.01	2.69 ± 0.01	0.37 ± 0.01	II	88.1
			Doublet II	0.50 ± 0.03	0.84 ± 0.05	0.42 ± 0.08	III	11.9
—	8	298	Doublet I	1.12 ± 0.01	2.12 ± 0.01	0.34 ± 0.01	II	94.3
			Doublet II	0.48 ± 0.03	0.59 ± 0.06	0.25 ± 0.09	III	5.7

[a] Isomer shift (relative to α-Fe).

[b] Quadrupole splitting.

[c] Full line width at half maximum.

[d] Partial resonant absorption areas of spectral components which represent relative contents of the corresponding forms assuming a common recoilless fraction for all forms.

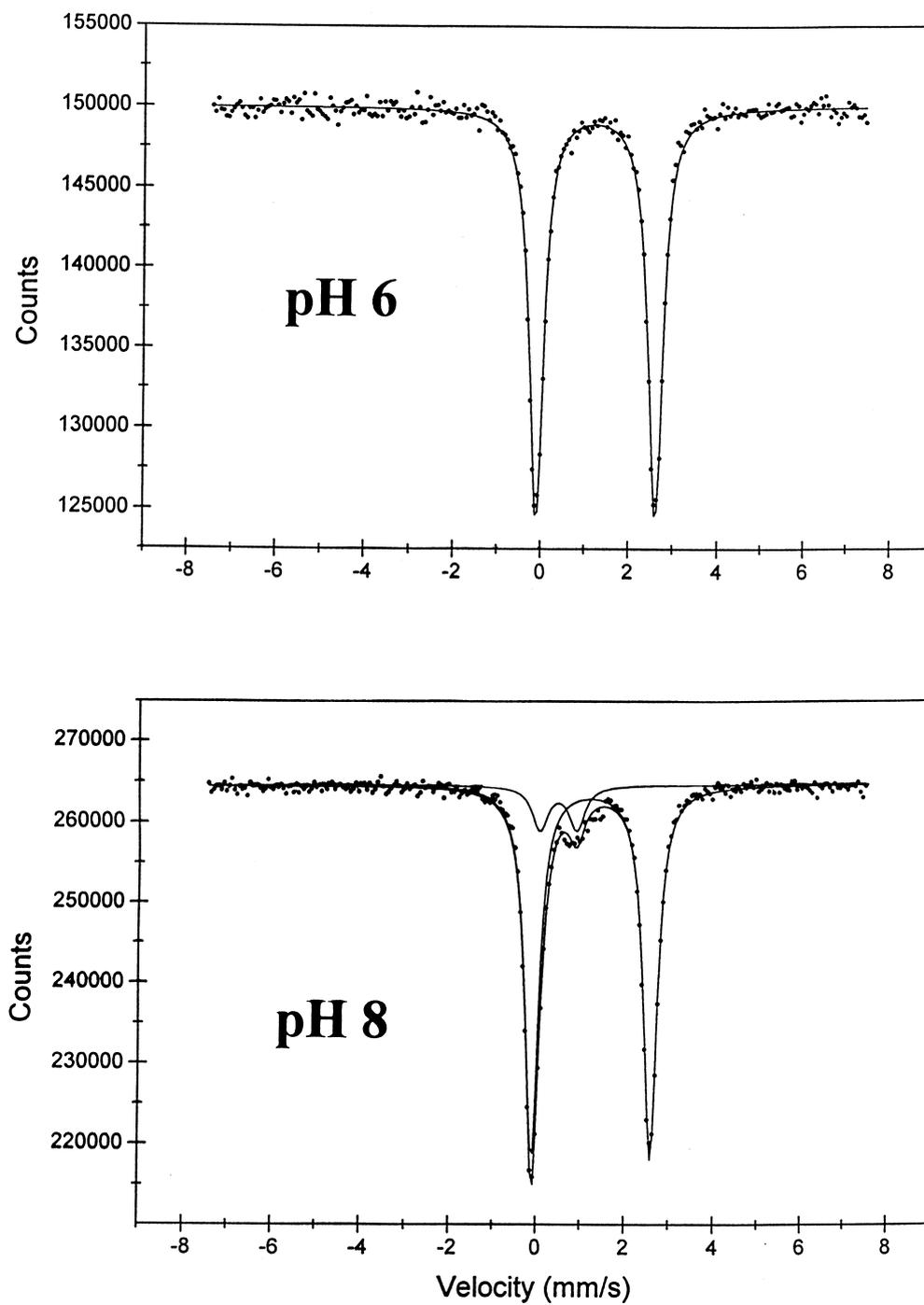[e] Aqueous suspension frozen 10 min after mixing (see Section 2.1.2).

Fig. 2. Mössbauer spectra of solid samples of iron(II) anthranilates precipitated at pH 6 and 8 (measured at $T = 80$ K; see also Table 1).

Fig. 3. Fourier transform infrared spectra of (a) anthranilic acid and (b) the products of its interaction with iron(II) at pH 6 (spectrum 1) and at pH 8 (spectrum 2) featured by the corresponding Mössbauer spectra shown in Fig. 2 (see also Table 1). Samples were pressed in pellets with spectroscopically pure KBr.

metal anthranilates), which is of analytical value for simultaneous direct determination of Fe^{II} and Fe^{III} [14], may well be related to their different coordination environment, structures and/or composition, as proposed by Dinsel and Sweet [14]. According to their chemical analyses, the solid ferric complex is believed to consist of an iron(III) atom coordinated by two anthranilate groups (obviously through the oxygen of the carboxylate group and the amino nitrogen each), one hydroxyl and one water molecule, whereas the ferrous species was found [14] to closely correspond to the formula $Fe(anthr)_2$, where $anthr = C_6H_4(NH_2)COO^-$. In the iron(III) complex, the coordinated water molecule might in principle be

exchanged for an oxygen-containing molecule of a nonaqueous solvent, thus accounting for the observed solubility of the resulting complex in the latter. This assumption, however, has to be proved by additional experiments which are in preparation.

Addition of $^{57}Fe^{III}$ nitrate to the excess of anthranilic acid in solution (up to the 1:3 metal-to-acid molar ratio) resulted in the formation of a turbid reddish-brown suspension indicating precipitation of iron(III) anthranilate (final pH about 5). After 10 min, a portion of the latter mixture was frozen and its Mössbauer spectrum at 80 K was obtained in order to detect the iron species formed (Fig. 1).

It can be seen from Fig. 1 that the spectrum is a superposition of three quadrupole doublets, the parameters of which are presented in Table 1. The main intensive doublet I with IS = 0.51 mm/s and QS = 0.71 mm/s is characteristic of iron(III) in the distorted octahedral coordination [16,17] and may be attributed to the iron(III) anthranilate complex in aqueous suspension. The obvious asymmetry of the coordination environment of the complex accounts for its relatively high QS value (0.71 mm/s). Note that a similar distorted octahedral coordination of high-spin iron(III) through both amino and carboxylic groups in its complexes with some amino acids was also assumed in [19] on the basis of Mössbauer spectroscopic data.

There is also clear evidence for the presence of two forms of iron(II) species represented by doublets II and III (see Fig. 1 and Table 1). As there was no iron(II) in the initial $^{57}Fe^{III}$ nitrate solution, this finding directly evidences that anthranilic acid slowly reduces iron(III) in aqueous medium at about pH 5 with the formation of iron(II) species [10]. This process was assumed [8] as a route for making virtually insoluble iron(III) present in soil available for the bacterium *Rhizobium leguminosarum* which was found to secrete solely anthranilic acid as an iron-solubilizing agent under iron deficiency. Under such conditions, anthranilic acid may in principle be oxidized to benzidine-3,3'-dicarboxylic acid [20] (which, considering its structure, could similarly coordinate iron).

The former of the two iron(II) species featured by the less intensive doublets II and III (see Fig. 1 and Table 1) is definitely Fe^{2+} (aqua complex) according to its Mössbauer parameters [16,17] (see Table 1),

while the latter is probably ferrous anthranilate complex. In order to validate this, we measured also Mössbauer spectra of solid iron(II) anthranilate precipitated as described earlier (see Section 2.1.1) at pH 6 (Fig. 2). Both at ambient (data not shown) and at liquid nitrogen temperature each of the spectra contains one very well resolved symmetric doublet with the parameters characteristic of high-spin iron(II) chelated by both N and O donor atoms [16,19] (see Table 1). Hence, minor doublet III in Fig. 1 may be attributed to iron(II) anthranilate. As its concentration calculated using the corresponding S_r value (see Table 1) was about 3×10^{-4} M, it might have been in solution rather than in aqueous suspension. Thus, its increased IS value (1.61 against 1.25 mm/s for solid sample at 80 K; see Table 1) may be attributed to the effect of hydration [16,17], though its low intensity and overlapping with doublets I and II could in principle have induced an additional error in the calculated parameters. Note that the dissolved iron(II) complex might have a higher coordination number (due, for example, to additional hydration), e.g. 6 instead of 4 assumed for solid ferrous anthranilate [14], which would also result in a higher IS [21].

Hence, it is concluded that in slightly acidic nitrate solutions (pH about 5) under aerobic conditions ferric ions can be gradually reduced by AA, which may have some ecological significance [8–11]. In particular, it should be noted that poorly soluble soil iron(III), which may thus be solubilized by AA involving a primary reduction step, is converted into the form of iron(II) which is much more generally bioavailable, whereas the common mechanism being realized by the majority of microorganisms under iron limitation involves the excretion of siderophores, and it is common knowledge that iron(III) chelated by a siderophore is often metabolically available only to those cells which possess specific cell surface receptors (proteins) for that particular siderophore [22]. The latter siderophore-mediated mechanism includes an iron(III) reduction step as well, which, however, takes place either at the surface or inside the cell using physiological reducing agents, thus releasing the resulting iron(II) cation which can be further utilized by the cell [1,22].

The reducing capability of AA is most probably effective also at pH 6, which is indirectly confirmed by the virtual absence of iron(III) impurities during

precipitation of iron(II) anthranilate in air at pH 6, as evidenced by Mössbauer spectroscopy (see Fig. 2). However, a similar sample precipitated at pH 8 (see Fig. 2) gives a composite spectrum containing an identical intensive symmetric doublet of iron(II) anthranilate with virtually the same parameters as that for pH 6 (see Table 1) both at ambient (data not shown in Fig.) and liquid nitrogen temperature, and also a minor component doublet with the IS and QS corresponding to high-spin iron(III) as a result of iron(II) oxidation in air at pH 8. (It should be noted that somewhat different relative fractions of the latter component, being 5.7% at 298 K and 11.9% at 80 K (see Table 1) may be explained both by experimental errors and, at least in part, by possible different temperature dependence of the Mössbauer effect for the ferrous and ferric species [21]). Thus, it may be concluded that, as in circumneutral media the iron(III) reduction process is generally known to be retarded, precipitation of iron(II) anthranilate at pH 8 in air results in the formation of a small admixture of ferric species.

In order to characterize the functional groups of AA involved in the complexation with iron cations, we compare FTIR spectra of AA [Fig. 3(a)] and the products of its interaction with iron(II) at pH 6 and 8 [Fig. 3(b); spectra 1 and 2, respectively] featured by the corresponding Mössbauer spectra shown in Fig. 2 (see also Table 1).

It should be noted that the frequencies in the spectrum of AA obtained in KBr pellet [see Fig. 3(a)] generally correspond to those for the AA crystal form I (stable under 81°C [15]) reported for its IR spectrum in mineral oil [23,24]. This is indirectly indicative of a negligible effect of pressing with KBr on its molecular H-bonding system, which may, however, not always be the case [25,26].

Comparing the AA spectrum in Fig. 3(a) with spectra 1 and 2 in Fig. 3(b), the latter being almost identical, one can note the following major changes involving the amino and carboxylic groups of AA upon its interaction with Fe^{II}:

the characteristic $\nu_{as}(NH_2)$ and $\nu_s(NH_2)$ bands of AA at 3325 and 3240 cm^{-1}, respectively, are non-symmetrically shifted to 3310 and 3143 cm^{-1} (the weaker band at 3220 cm^{-1}, which is also seen in

Fig. 3(b), may probably be attributed to some kind of $\nu(N–H\cdots)$ association);

the broad intensive $\nu(OH)$ envelope related to the associated carboxylic group in AA (including also a contribution from the fraction of AA molecules in the zwitterionic form), centred at ca. 2560 cm^{-1} [see Fig.3(a)], practically disappears, as well as the $\nu(C=O)$ band at 1662 cm^{-1}, a number of strong COOH-related bands at about 1200–1380 cm^{-1} [15,23,27] (except the evidently less affected medium $\nu(C–N)$ band at 1320–1324 cm^{-1} [15]), including in-plane $\delta(OH)$ at 1371 cm^{-1}, and the very strong out-of-plane $\gamma(OH)$ band in AA at 933 cm^{-1};

there appears the characteristic couple of bands featuring asymmetric $\nu_{as}(COO^-)$ and symmetric $\nu_s(COO^-)$ stretching modes of carboxylate at 1542 and 1407 cm^{-1}, respectively [see Fig. 3(b)]; the strong deformational COOH band in AA at 658 cm^{-1} decreases in intensity and shifts to 634 cm^{-1} [$\delta(COO^-)$], whereas the narrow band adjacent to it at ca. 667 cm^{-1}, featuring the $\delta(CCC)$ mode in AA, remains unchanged [see Fig. 3(b)]; the strong and evidently complex band with a significant contribution from the $\delta(NH_2)$ mode at 1581 cm^{-1} in AA [see Fig. 3(a)] transforms to the narrow well-resolved bands at 1615 and 1591 cm^{-1} [see Fig. 3(b)]; the latter band featuring the $\nu(CC)$ ring mode is active in IR for only substituted aromatic rings for the reasons of symmetry [27]; also, the relatively intensive band at 1139 cm^{-1} and the narrower band at 544 cm^{-1}, featuring the $r(NH_2)$ and $\gamma(NH_2)$ modes in AA, respectively [15] [see Fig. 3(a)], practically disappear.

One may note also the unaffected very strong typical out-of-plane $\gamma(CH)$ band of the benzene ring at 754–752 cm^{-1} [see Fig. 3(a) and (b)] and the neighbouring strong $\gamma(C–NH_2)$ band in AA at 772 cm^{-1} [see Fig. 3(a)] which possibly shifts to 717 cm^{-1} upon Fe^{II}–N coordination [see Fig. 3(b)].

The aforementioned spectroscopic characteristics observed in going from AA to its iron(II) complex unambiguously show that both the carboxylic group and the amino group of AA are directly involved in coordination with Fe^{II}.

The iron(III) impurity, appearing in the ferrous

anthranilate sample precipitated at pH 8, featured by the weak narrow Mössbauer doublet (see Fig. 2 and Table 1), is, most probably, a hydrolysed ferric species rather than ferric anthranilate, as the latter would have been removed during washing with acetone [14] (see Section 2.1.1). Also, its QS value (0.84 mm/s at 80 K; see Table 1) is noticeably higher than that for ferric anthranilate (0.64 ± 0.08 mm/s at 80 K) reported in [28], while its parameters are quite typical for dried ferric hydroxide [16,17,21]. [Note that in aqueous suspension the QS value for ferric anthranilate (see doublet I in Fig. 1 and Table 1), being 0.71 mm/s at 80 K, may be a result of hydration]. Thus, the weak additional absorption at ca. 460 cm^{-1} in spectrum 2, as compared to spectrum 1[see Fig. 3(b)], probably represents the ν(Fe–O) or δ(O–Fe–O) modes (which are most intensive and typical for ferric oxyhydroxides [29]) for the admixture of hydrolysed ferric species in the anthranilate matrix.

4. Conclusions

Using Mössbauer spectroscopic measurements, it has been shown that in slightly acidic nitrate solutions (pH 5) under aerobic conditions ferric ions can still be gradually reduced by AA, which may have some ecological significance consisting in a possible increase in bioavailability of poorly soluble soil iron(III) by a mechanism different from that involving bacterial siderophores. However, in circumneutral and slightly alkaline media this process is retarded, and iron(II) anthranilate precipitated at pH 8 in air contains hydrolysed ferric species. Mössbauer parameters have been calculated for iron(II) and iron(III) anthranilates in aqueous medium and for solid phases. The FTIR data obtained for ferrous anthranilates, as compared to anthranilic acid, definitely exhibit the direct involvement of both the carboxylic and the amino groups of anthranilic acid in coordination with the iron cation.

Acknowledgements

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