

Spectroscopic investigation of indole-3-acetic acid interaction with iron(III)

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Abstract

Fe^{III} was found to be gradually reduced by indole-3-acetic acid (IAA) in slightly acidic nitrate solution with further re-oxidation of the resulting Fe^{II} upon drying in air, which is reasoned to be of ecological significance considering IAA excretion by many soil micro-organisms. Fe^{III}-IAA complex was isolated; its composition, some physicochemical properties and structural aspects were studied using Mössbauer, FTIR spectroscopic and other techniques. Possible influence of Fe^{III} coordination on the redox properties of the ligand is also considered from the viewpoint of the nature of the bonding system which involves the conjugated π -electronic system of the pyrrole cycle along with the carboxylic O-donor atom. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Indole-3-acetic acid (IAA) is a phytohormone of the auxin series; its biosynthesis, besides higher plants, is also performed by a number of soil micro-organisms, and in particular, plant growth-promoting rhizobacteria [1,2]. This process, being an important component of plant-microbe interactions, accounts for plant growth regulation controlled in part by the amounts of IAA excreted by soil micro-organisms into the environment [3,4]. The IAA level is thought to be regulated by its oxidative degradation involving

plant peroxidases and/or by photochemical oxidation giving similar products [1,5,6]. The formation of a triple complex (peroxidase-IAA-oxygen) has been proposed for the IAA oxidative degradation mechanism including as a key step the Fe³⁺ \rightarrow Fe²⁺ transition in the enzyme form [6]. Iron was also demonstrated [7,8] to be essential for enzymatic transformation of anthranilic acid, a key intermediate in the biosynthesis of L-tryptophan which, in its turn, is the main metabolic precursor of IAA [2,3]. The latter excreted into soil in noticeable quantities [1–4] can also interact with various soil components including metal ions. This may be of certain ecological significance, in particular, for iron(III) which is usually abundant in soil yet being virtually insoluble in the ferric form over a wide pH range, but can be

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Table 1

Mössbauer parameters (Errors (in the last digits) are given in parentheses) of iron(III)-containing solutions of IAA stored for various periods of time before rapid freezing in liquid nitrogen (1, 2), of the dried residue (3) and solid iron(III)–IAA complex (4)

Sample	<i>T</i> (K)	Component	IS ^a (mm/s)	QS ^b (mm/s)	LW ^c (mm/s)	<i>S_r</i> ^d (%)	Figure
1. Fe ^{III} –IAA solution frozen 25 min after mixing	80	Fe ^{II}	1.39(2)	3.30(5)	0.41(8)	28.0	–
2. Fe ^{III} –IAA solution frozen 2 d after mixing	80	Fe ^{II}	1.37(1)	3.31(2)	0.42(2)	97.3	1(1)
3. Sample 2 dried in air at room temperature	80	Fe ^{III}	0.48(1)	0.70(2)	0.69(2)	100	1(2)
4. Solid Fe ^{III} –IAA complex	298	Fe ^{III}	0.38(1)	0.78(1)	0.49(2)	100	1(3)

^a Isomer shift (relative to α -Fe).

^b Quadrupole splitting.

^c Full line width at half maximum.

^d Relative resonant absorption areas of the relevant spectral components, which represent relative contents of the corresponding Fe forms assuming a common recoilless fraction for all forms in a sample, if more than one.

reductively solubilised under appropriate conditions [8–11].

In the present work, IAA interaction with iron(III) was investigated in aqueous solution, and iron(III)–IAA complex was isolated and characterised using Mössbauer, Fourier transform infrared (FTIR) spectroscopic and other techniques. The effects of iron(III) coordination on the π -electronic bond system of the ligand are also discussed.

2. Experimental

2.1. Sample preparation

2.1.1. Iron-containing aqueous solutions

For Mössbauer measurements in aqueous media, iron(III) nitrate solution was prepared by dissolving 95.6% enriched ⁵⁷Fe metal (Centre for Radionuclide Diagnostics at the Russian Foundation for Basic Research, Moscow) in a slight excess of 50% nitric acid (analytical purity) as described earlier [10]. The absence of Fe^{II} in the 0.1 M stock solution was confirmed by special Mössbauer measurements. The concentrations of iron(III) and IAA (Eastman Kodak, chemical purity) in the solution under study were adjusted to 0.01 and 0.03 M, respectively, (pH ca. 4.5). The mixture was allowed to stand at room temperature for a certain period of time and then rapidly frozen by adding it dropwise into a sample holder cooled with liquid nitrogen.

2.1.2. Solid iron(III)–IAA complex

Iron(III) nitrate solution was prepared from metal powder (natural Fe reduced in hydrogen atmosphere; pharmacological purity) as described above. 0.15 g (0.84 mmol) of IAA was dissolved in bidistilled water at 60°C under permanent stirring, partly neutralised with 0.1 M KOH up to pH 6 and then slowly and gradually mixed with 0.03 M iron(III) nitrate solution up to the final Fe-to-IAA molar ratio of 1:3. The solution rapidly grew coloured (pink), and in a few minutes a cocoa-reddish precipitate of the iron(III)–IAA complex was noticeable. It was filtered, rinsed with a dilute solution of NaHCO₃ to remove possible residuals of free IAA, washed well with bidistilled water and dried under vacuum (3 Torr) for 25 min.

Elemental analysis gave the following results. Found (%): C, 64.71; H, 4.82; and N, 7.63. Calculated for the net formula Fe(C₁₀H₈NO₂)₃: C, 62.22; H, 4.14; and N, 7.25.

For Mössbauer measurements, a portion of the complex was redissolved in acetone (Sigma, chemical purity) to separate it from any possible Fe^{III} oxide-containing admixtures which might contribute to the spectrum, filtered and dried at room temperature, which did not affect the appearance and properties of the amorphous powdered product.

2.2. Mössbauer spectroscopic measurements and data treatment

Mössbauer spectra acquisition and data treatment

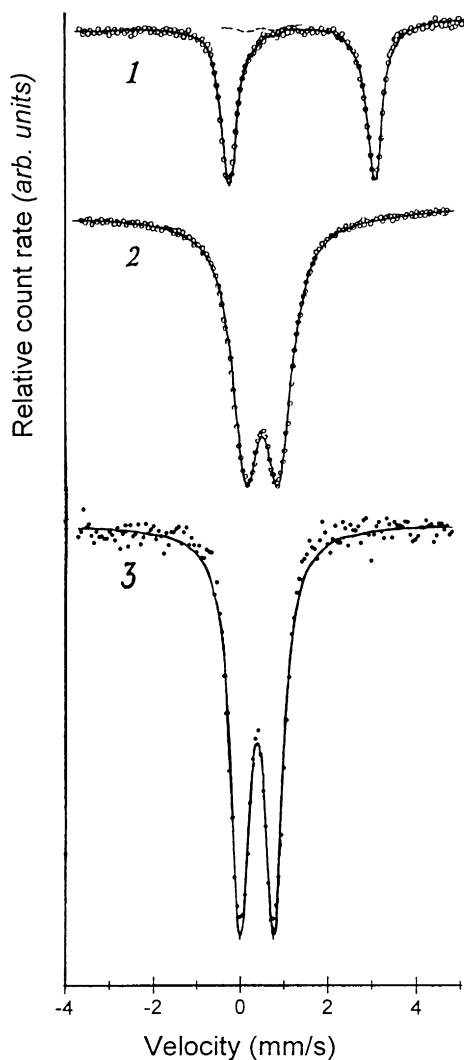


Fig. 1. Mössbauer spectra of: (1) iron(III)-containing solution of IAA frozen 2 d after mixing; (2) the solid residue obtained after drying the solution in air; and (3) isolated iron(III) complex with IAA (see also Fig. 2(a) and Table 1, samples 2–4) measured at $T = 80$ K. Solid lines represent the resulting spectra composed of calculated Lorentzian-shaped components computer-fitted to the experimental data (points).

were described in detail elsewhere [10,11]. Standard PC-based statistical analysis included fitting the experimental data obtained to a sum of Lorentzian-shaped component lines with a least squares fit, which enabled calculation of the values of isomer shift (IS; relative to α -Fe), quadrupole splitting (QS), linewidth

(i.e. full width at half maximum, LW) and relative areas of spectral components.

2.3. Vibrational spectroscopic measurements and data treatment

Infrared spectrum of the iron(III)–IAA complex (see Section 2.1.2) was obtained in the diffuse reflectance infrared Fourier transform (DRIFT) mode using a Nicolet spectrometer (model Magna IR 750; DTGS detector; Nichrome source; beamsplitter: KBr) with a total of 100 scans; resolution up to 4 cm^{-1} . A small portion of the sample (ca. 0.2 mg) was carefully ground with ca. 15 mg of spectroscopically pure KBr (Merck) and placed into a Micro sampling cup (Spectra-Tech Inc.). Spectra were recorded using a Spectra-Tech diffuse reflectance accessory against a KBr background. The same apparatus was used for obtaining FT-Raman spectra of IAA (FT-Raman accessory; a Nd^{3+} -YAG laser, 1064 nm excitation wavelength with a ca. 0.5 W laser power at the sample and a total of 100 scans applied; InGaAs detector; beamsplitter: CaF_2), for which ca. 40 mg of the latter was pressed in an NMR tube (4 mm internal diameter), attached to the sample holder, and the laser beam was focussed at the centre of the sample. (It appeared impossible to obtain a satisfactory FT-Raman spectrum of the iron(III)–IAA complex under study even at lower laser power values and in KBr mixtures owing to immediate local decomposition of the sample). Treatment of the spectra was performed using the OMNIC 3.1 software (Nicolet) accompanying the equipment. FTIR spectrum of IAA was obtained in a pellet pressed with KBr (Merck; spectroscopic purity) following the standard procedure described in detail earlier [10]. If not indicated otherwise, all measurements were performed at ambient temperature (295 ± 3 K).

3. Results and discussion

3.1. Long-term interaction of indole-3-acetic acid with iron(III) in aqueous solution

Interaction of IAA with iron(III) in slightly acidic nitrate-containing aqueous solutions in air was found to result in the formation of iron(II) which slowly and gradually accumulated in the solution with time. This

was confirmed by Mössbauer spectroscopy which showed the appearance of a high-spin Fe^{II} component; its content represented by the relative spectral area of the iron(II) quadrupole doublet reached 28% of the total iron in 25 min (Table 1, sample 1), and two days after mixing the mixture contained virtually only iron(II) (Fig. 1(1); see also Table 1, sample 2). The Mössbauer parameters of samples 1 and 2 in Table 1 are quite similar and very close to those reported for iron(II) aqua complex [12,13] which indicates that iron(II), formed in the course of gradual iron(III) reduction by IAA in this slightly acidic solution, is in its hydrated form and not directly coordinated to IAA. The gradual reduction of Fe^{III} by IAA in solution, similar to that reported also for a few other organics of biological origin and, in particular, metabolites of soil micro-organisms [9–11,14], owing to a higher general solubility and, therefore, bioavailability of the resulting Fe^{II} , may be of ecological importance, especially for weakly acidic soils (pH \sim 4–5) which constitute over 30% of only arable territories [15].

When the deeply coloured solution obtained after long-term storage (see Table 1, sample 2) was allowed to dry in air at ambient temperature, the resulting dark-purple solid gave an intensive symmetric quadrupole-split doublet with somewhat broadened lines (Fig. 1(2), Table 1, sample 3) with the parameters typical for high-spin Fe^{III} in essentially distorted octahedral coordination [13]. Thus, iron(II) is reoxidised in air upon drying under these conditions. This process, which is similar to the cyclic processes in Fe^{III} –adriamycin complexes with particular chelation structures [16] leading to molecular oxygen reduction, could facilitate oxidative degradation of IAA in soil in the presence of iron(III) under appropriate conditions [11]. Note that some noticeable line broadening (see Table 1, sample 3) in this case is most probably connected with the presence of IAA oxidation products [17] which could similarly coordinate Fe^{III} as well, giving very close parameters (IS and QS), resulting in their slight distribution.

3.2. Indole-3-acetic acid complex with iron(III)

Elemental analysis (see Section 2.1.2) shows that the composition of the complex obtained corresponds to tris-(indole-3-acetato)iron(III) $\text{Fe}[(\text{C}_8\text{H}_6\text{N})\text{CH}_2\text{COO}]_3$. The complex was found to be poorly soluble in water and well soluble in oxygen-containing organic solvents (ethanol, isopropanol, acetone), in contrast to, e.g. CCl_4 . Thus its solubility obviously cannot be connected with an exchange of ligands which was quite reasonably assumed (though not yet checked experimentally) for similarly obtained Fe^{III} anthranilate complex [18] with the composition $\text{Fe}[(\text{A})_2(\text{H}_2\text{O})\text{OH}]$, where A = anthranilate. In the latter complex, the inner-sphere water molecule was supposed to be exchangeable for an oxygen-containing molecule of an organic solvent, accounting for its solubility in the latter (note that iron(II) anthranilate $\text{Fe}[\text{A}]_2$ [10,18] and some other divalent metal (M^{II}) anthranilates of the same composition $\text{M}^{\text{II}}[\text{A}]_2$ are insoluble in O-containing organics [18]).

Room-temperature Mössbauer spectrum of the iron(III)–IAA complex obtained consists of a well-resolved symmetric quadrupole doublet (Fig. 1(3)) with the parameters (Table 1, sample 4) corresponding to high-spin iron(III) in a distorted octahedral coordination [13] indicated by its rather large QS value (0.78 mm/s). This is even higher than 0.60–0.69 mm/s (at 298 K) reported for distorted octahedral high-spin Fe^{III} amino acid complexes with mixed N- and O-donor atoms [19]. However, its IS value (0.38 mm/s) is close to those for most of the latter. For comparison, for ferric anthranilate $\text{Fe}[(\text{A})_2(\text{H}_2\text{O})\text{OH}]$ with a distorted octahedron of two N- and four O-donor atoms around the Fe^{III} ion [18], $\text{QS} = 0.64 \pm 0.08$ mm/s at 80 K [13] (note that freezing in liquid nitrogen often leads to higher QS values owing to an enhanced rigidity of the structure [13,19]), whereas for the pentacoordinated ferric complex with an essentially lower coordination symmetry, $\text{Fe}[(\text{A})_2\text{Cl}]$, $\text{QS} = 1.76$ mm/s at 300 K [20].

The above mentioned data can be interpreted

Fig. 2. FTIR spectra of: (a) isolated iron(III) complex with IAA (see also Fig. 1(3) and Table 1, sample 4) in the DRIFT mode; and (b) IAA, both obtained in KBr mixtures; and (c) FT-Raman spectrum of IAA.

considering the planar conjugation of the non-shared electron pair of the N atom in the IAA pyrrole ring with the π -electrons of the 2,3-double bond [21] which, in contrast to the ‘basic’ N atom in, e.g. amino acids, prevents direct coordination of the IAA heteroatom with Fe. In this case, considering the composition of the complex and the octahedral coordination of the ferric cation proposed above, it could be reasoned that either the latter is coordinated by three ionised carboxylate fragments of the IAA side chain (six O-donor atoms) or, in view of a more probable high covalency of the Fe^{III}-O bond, iron(III) is coordinated, along with the carboxylic oxygen, by the conjugated π -electronic system. The former case (identical donor atoms) would probably give an essentially smaller QS [22] than that observed (see Table 1, sample 4) owing to a higher coordination symmetry.

In order to clarify the structure and coordination of the Fe^{III}-IAA complex, we used FTIR spectroscopy to compare the spectra of the complex (Fig. 2(a)) and of IAA (Fig. 2(b)); its FT-Raman spectrum is also given in Fig. 2(c)). It can be seen that the characteristic ν (N-H) mode of the indole moiety, which in IAA is featured by a very strong sharp IR band (Fig. 2(b)) and a weaker Raman peak (Fig. 2(c)) both appearing at 3390 cm⁻¹, in the complex transforms into a broadened asymmetric strong band centred at 3403 cm⁻¹ (see Fig. 2(a)). Note that the direct formation of a N-metal coordination bond decreases the ν (N-H) vibration frequency [10,23].

Also, the band assigned to the out-of-plane γ (N-H) wagging mode, which for IAA is very weak in Raman but gives a strong sharp IR band at 517 cm⁻¹ (see Fig. 2(b) and (c)) and is typical for indole (500 cm⁻¹ in the solid state) and pyrrole as well [24], broadens and markedly decreases in intensity in the complex (see Fig. 2(a)). However, the typical benzene ring vibration bands in IAA, e.g. strong out-of-plane γ (C-H) at 740 cm⁻¹ (761 cm⁻¹ in Raman); in-plane δ (C=C) at 1457 cm⁻¹ (strong in IR but weaker in Raman); two ν (C=C) bands at ca. 1558 and 1620 cm⁻¹, remain virtually unchanged both in position and intensity in going to the IAA-Fe(III) complex (see the corresponding bands at 746, 1460 and 1619 cm⁻¹ with a shoulder at ca. 1560 cm⁻¹ in Fig. 2(a)). These effects provide evidence for the involvement of the IAA pyrrole moiety in coordi-

nation and, on the other hand, show that the benzene ring in IAA is not involved in coordination with Fe^{III}, which, as proposed earlier, is likely to involve π -electrons of the pyrrole ring conjugated with the non-shared electron pair at the heteroatom [25].

Though Fe^{III} coordination with the IAA carboxylic group is undoubted (see, e.g. smoothening of the carboxylic ν (OH) region 2800–2400 cm⁻¹ and disappearance of the broadened γ (OH) band at 905 cm⁻¹ in IAA upon coordination; cf. Fig. 2(a) and (b)), the typical strong ν (C=O) band in IAA at 1703 cm⁻¹ (see Fig. 2(b)) does not disappear in the complex like it disappears in many carboxylates featured by the formation of largely ionic (COO⁻)-metal (or ammonium) bonds [10,23], but rather undergoes a slight blue shift to 1710 cm⁻¹ (see Fig. 2(a)) and somewhat decreases in intensity. Thus there is certain inequality between the oxygen atoms, as Fe^{III} is coordinated through only one O-donor atom of the IAA side-chain carboxyl. Note that the ν (Fe-O) mode (see the composite band at about 520–460 cm⁻¹ with a centre at 490 cm⁻¹; Fig. 2(a)), which is observed at lower frequencies than, e.g. 535–560 cm⁻¹ for hexacoordinated tris-(malonato)ferrates(III) with alkaline outer-sphere cations [26], also evidences for a higher covalency of the Fe-O bond in the Fe^{III}-IAA complex. In our opinion, the band at 490 cm⁻¹ is likely to feature the ν (Fe-pyrrole ring) vibrations (cf. a similar Fe-ring mode in ferrocene featured by an IR band at 478 cm⁻¹ and the like in other compounds [27]).

It can thus be reasoned that indole-3-acetate chelates Fe^{III} via its carboxylic oxygen and the π -electronic system of the pyrrole ring forming a quasi-six-membered ring for each ligand, considering possible variable orientations of the IAA side chain towards the indole plane [28]. The obvious inequality of the coordination bonds and possible steric effects may account for a significant coordination asymmetry resulting in the marked QS value (see Table 1, sample 4).

The conclusion about the involvement of the π -electronic system of the pyrrole ring in coordination with Fe^{III} is consistent with the data of our ¹H NMR and UV-Vis studies of IAA and its iron(III) complex [29] in organic solvents. In particular, resonant signals of the IAA aromatic protons (at ca. 7.5 ppm; in

deuterated acetone) were shown to shift by 0.3–0.5 ppm towards strong fields upon coordination which could shift the π -electronic density to the metal ion, thus decreasing the ring π -current and altering the spatial π -electronic density distribution.

Electronic absorption spectra of IAA (in ethanol solutions) showed intensive π – π^* -transition bands with $\lambda_{\max} = 219$ nm ($\log \varepsilon = 4.79$) and 280 nm (4.11) with no absorption in the visible region [29]. For the IAA–Fe^{III} complex, both the π – π^* -transition bands showed a hyperchromic effect with a slight red shift of the former: $\lambda_{\max} = 223$ nm (4.93) and 280 nm (4.43). These changes evidence for the involvement of the IAA π -electronic system in coordination. In the spectrum of the complex, there also appeared a new band in the UV region with $\lambda_{\max} = 337$ nm ($\log \varepsilon = 3.77$) related to charge transfer. The indole moiety in tryptophan was also assumed [30] to be involved in coordination with Fe^{III} with charge transfer. In addition, the IAA–Fe^{III} complex shows [29] two d–d^{*}-transition bands related to the coordinated ferric cation with $\lambda_{\max} = 410$ nm ($\log \varepsilon = 2.94$) and 516 nm (2.73).

Note that several IAA (L[–])–lanthanide (Ln³⁺) complexes of the formula LnL₃ × 3H₂O were found [31] to exert an even stronger auxin effect than that of IAA (or of LnCl₃), which is obviously a result of the influence of metal coordination on the physiological activity of IAA.

4. Conclusions

IAA was found to gradually reduce Fe^{III} in slightly acidic nitrate solution; the resulting Fe^{II} was re-oxidised upon drying in air. These processes are reasoned to be of ecological significance considering IAA excretion by many soil micro-organisms [1–4]. The type of IAA–Fe^{III} coordination considered involving the π -electronic system of the IAA pyrrole ring, which in indole derivatives is known to be more prone to oxidation than the benzene cycle [32–34], may well influence the redox properties of the indole moiety and thus alter the kinetics and/or mechanism of (photo)chemical and enzymatic processes of IAA oxidative degradation [5,6]. This corresponds to the fact that aerobic photo-oxidation of the double bond in the pyrrole cycle of indole derivatives is catalysed by

Fe³⁺ [33]. Such processes may well occur abiotically in soil where IAA and its derivatives may be in direct contact with iron(III).

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