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Synthesis and characterization of 2-indolehydroxamic acid and its solid complex with iron(III)

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Abstract

The synthesis and some physicochemical properties of 2-indolehydroxamic acid (2-IHA) and Fe(III)-2-indolehydroxamic acid solid complex (Fe(III)-2-IHA) are described. Both substances have been characterized by chemical analysis, IR and NMR spectroscopy and thermogravimetric analysis.

INTRODUCTION

Many hydroxamic acids have been studied as analytical reagents of inorganic ions [1–2].

2-Indolehydroxamic acid (2-IHA) has been synthesized by us and its reactivity with inorganic ions is reported. 2-IHA reacts with Fe(III) giving a violet colour in acid medium that can be extracted in toluene–adogen [3], a yellow colour in basic medium, and a less soluble red complex in the pH range 3.0–9.0. In recent years, some papers about characterizations of solid complexes of hydroxamic acids with metallic ions have been published [4–6].

In this paper, the synthesis and some properties of 2-IHA and Fe(III)-2-indolehydroxamic acid solid complex (Fe(III)-2-IHA) are described.

EXPERIMENTAL

Reagents

2-IHA was synthesized from 2-ethyl-2-indolecarboxylate and hydroxylamine hydrochloride, which were purchased from Sigma.

Iron(III) solutions were prepared from $Fe(NO_3)_3 \cdot 9H_2O$ (Merck) and

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standardized gravimetrically. All compounds were of analytical reagent grade and the aqueous solutions were prepared using distilled water from a Milli-Q water purification system.

Apparatus

UV–vis spectra were recorded on a Beckman DU-50 spectrophotometer with 1.0 cm glass or quartz cells, interfaced via RS-232 to an IBM personal computer. The control of the instrument and the analysis of spectrophotometric data have been performed with the DATA LEADER software package [7].

Elemental analyses were carried out on a Perkin-Elmer 240 analyzer.

IR and NMR data were recorded using a Perkin-Elmer 339 IR spectrophotometer and a Perkin-Elmer R-32(90 MHz) spectrometer, respectively.

Thermal studies were performed with a Mettler MTA-3000 system consisting of a Mettler TG 50 thermobalance and a Mettler differential scanning calorimeter.

Synthesis of 2-IHA

2-IHA was synthesized according to the following procedure. First, we obtained the potassium salt of 2-IHA, by mixing in ethanol 2-ethyl-2-indolecarboxylate with free hydroxylamine, which had been generated by treating hydroxylamine hydrochloride with KOH in ethanol. The mixture was stirred for 48 h at room temperature. The yellowish precipitate was filtered and washed successively with ethanol until there was no alkaline reaction. Finally, 2-IHA was obtained by dissolving the potassium salt of 2-IHA in 2 N acetic acid at 35–40°C. The resulting solid (60% yield) was washed with cold water and dried over calcium chloride.

Synthesis of Fe(III)-2-IHA solid complex

The metal chelate was prepared as follows. More than 25 ml of an aqueous solution (1.0×10^{-2} M) of 2-IHA was added to 25 ml of 2.5×10^{-3} M Fe(III) solution at pH 5–7. The mixture was shaken for 30 min at 40–45°C. The red precipitate obtained was immediately filtered off, washed with ethanol:H_2O (1:1) and dried over calcium chloride.

RESULTS AND DISCUSSION

Elemental analysis

Elemental analyses of 2-IHA, its potassium salt and Fe(III)-2-IHA complex were determined under the experimental conditions indicated above. The results obtained are collected in Table 1 and show good agreement with the theoretical data.

TABLE 1

Elemental analyses of 2-IHA ($C_9H_8N_2O_2$), potassium salt of 2-IHA ($KC_9H_7N_2O_2$) and Fe(III)-2-IHA complex ($Fe(C_9H_7N_2O_2)_2OH \cdot H_2O$)

Compound	C/%		H/%		N/%		H_2O/%[a]	
	C.	F.	C.	F.	C.	F.	C.	F.
$C_9H_8N_2O_2$	61.36	61.31	4.54	4.56	15.90	15.68		
$KC_9H_7N_2O_2$	50.47	53.67	3.27	3.79	13.08	13.88		
$Fe(C_9H_7N_2O_2)_2OH \cdot H_2O$	48.97	48.52	3.80	3.41	12.70	12.12	4.08	3.85

[a] Water percentage measured from TG data.

The Fe(III)-2-IHA chelate has 1:2 stoichiometry and contains a OH group similar to other Fe(III) complexes of hydroxamic acids [6].

2-IHA and its potassium salt are isolated without water of crystallization of coordination, but the Fe(III)-2-IHA complex has one molecule of water in its structure.

Thermal behaviour

The thermogravimetric curves (TG) of 2-IHA and Fe(III)-2-IHA were obtained in a dynamic air atmosphere, using sample masses of 11.54 mg and 12.21 mg, respectively, and at a heating rate of 10°C min^{-1}. The temperature range studied was 30–800°C.

The results obtained are shown in Figs. 1 and 2. TG of 2-IHA shows that

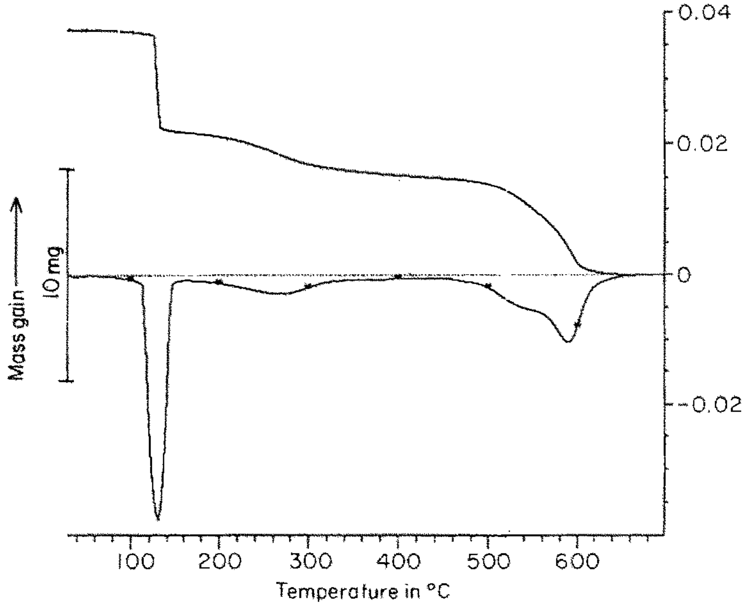

Fig. 1. Thermogravimetric curve of 2-IHA.

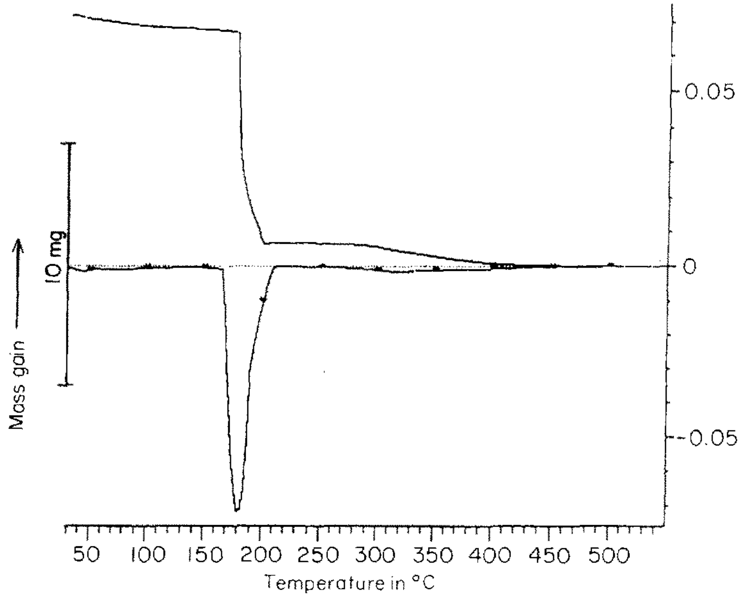

Fig. 2. Thermogravimetric curve of Fe(III)-2-IHA.

this reagent is anhydrous, and its thermal decomposition takes place by three steps between 100 and 650°C (Fig. 1). The first step (100–170°C) presents a 42.0% experimental mass loss that can probably be assigned to the loss of phenyl group (43.2% theoretical loss). The other two steps (between 170 and 650°C) lead to complete decomposition of the reagent, leaving no residue as expected.

The thermal behavior of the Fe(III)-2-IHA complex shows a TG curve with three steps (Fig. 2). The data for calculated and experimental mass loss, the temperature range, and the process assigned are given in Table 2. Again, there are good agreements between experimental and theoretical values. At the first stage, between 40 and 125°C, the mass loss indicates the

TABLE 2

TG assignations for the decompositions process of Fe(III)-2-IHA complex

Process assigned	Temp. range/ °C	Mass loss/%		T/°C[b]
		Calculated	Found	
$Fe(C_9H_7O_2N_2)_2OH \cdot H_2O \rightleftharpoons Fe(C_9H_7O_2N_2)_2OH$	40–125	4.08	3.85	–
$Fe(C_9H_7O_2N_2)_2OH \rightleftharpoons Fe(CO_2N)$[a]	150–220	70.10	71.40	–
$Fe(CO_2N) \rightleftharpoons Fe_2O_3$	250–500	7.70	7.73	650

[a] Empirical formulae. [b] Temperature at which the residue was measured.

elimination of one molecule of water from the complex. The anhydrous complex is stable over a short temperature range, and a strong decomposition in two steps is observed starting from 150°C to give finally a residue of the corresponding metallic oxide (above 500°C).

IR and NMR spectra

IR spectra of 2-IHA and Fe(III)-2-IHA complex were obtained as KBr pellets, and the corresponding absorption bands are given in Table 3. The bands of –CO–NH–OH and indole groups, amongst others, clearly support the structure of hydroxamic acid.

In 2-IHA a band appears at 1620 cm^{-1} assignable to C=O group (band amide I) [8]. This band is of low intensity probably due to carbonyl group participation in the formation of hydrogen bonds, and also the band is shifted to lower wavelength due to conjugation with the aromatic group. In the Fe(III)-2-IHA complex this band appears at 1590 cm^{-1} as consequence of the carbonyl–metal binding. Both compounds show a band of N–H group at 1560 cm^{-1} (amide II), and between 3000 and 3600 cm^{-1} other bands corresponding to –OH and –NH groups. As expected, these bands exhibit minor intensities in the complex.

The ^{1}H NMR spectrum of 2-IHA is shown in Fig. 3. At 11.6 and 11.3 ppm appear two singlets of the –OH and –NH protons, respectively, which are attributed to the hydroxamic group. The aromatic –NH proton appears at 9.2 ppm, downfield shifted, probably due to the electron withdrawing effect of the hydroxamic group at the α position [9]. These protons are easily interchanged when the spectrum is recorded in D_2O. The five aromatic protons appear as a multiplet between 7.6 and 7.0 ppm. The presence of the aromatic moiety was also confirmed by the ^{13}C NMR spectrum, which

TABLE 3

IR absorption bands in cm^{-1}

Compound		Group
2-IHA	Fe(III)-2-IHA	
3000–3500	3000–3600	N–H and O–H association
1620	1590	–CO– (amide I)
1560	1560	N–H (amide II)
1510		N–H (indole)
	1320	C–N (amide III)

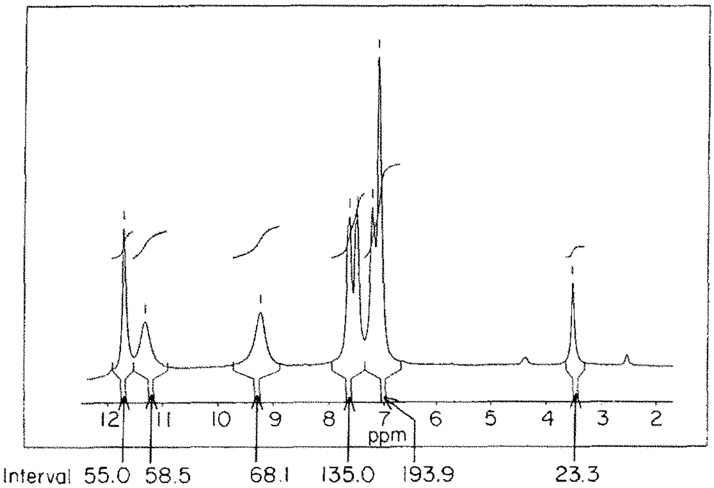

Fig. 3. ^{1}H NMR spectrum of 2-IHA.

shows eight carbon signals between 99 and 136 ppm, and the carbonyl group at 160 ppm.

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