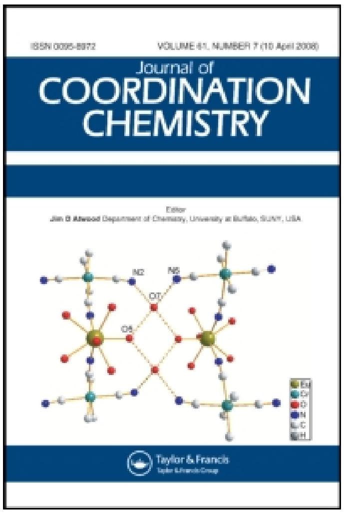

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BINUCLEAR COMPLEXES OF IRON(III) WITH SALICYLATE LIGANDS

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BINUCLEAR COMPLEXES OF IRON(III) WITH SALICYLATE LIGANDS

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Binuclear iron(III) complexes with salicylate ligands, $Na_2[Fe_2(C_7H_4O_3)_4(H_2O)_2]$ and $Na_4[Fe_2(C_7H_4O_3)_4(OH)_2]$, crystallize out in the pH range 1–5 and pH 5.5, respectively, from solutions containing iron(III) chloride and a slightly more than two molar proportion of sodium salicylate. Infrared and Mössbauer spectral results and magnetic moment data indicate the presence of non-linear Fe–O–Fe bridge bonds. Evidently two salicylate ligands form bridges between the two iron(III) ions through phenolic oxygen. Mössbauer spectral results indicate the absence of bridging salicylate ligands in solutions of the complex prepared by mixing iron(III) chloride and two to three-fold molar excess of salicylate ions; only mononuclear complexes exist in such solutions.

INTRODUCTION

Complex formation in aqueous solution between iron(III) ion and salicylate ligands is a relatively well explored area; depending on the pH of the solution complexes with iron(III) to salicylate ratio 1:1, 1:2 and 1:3 are formed.[1–6] But hitherto there has been no report on the isolation of any iron(III) salicylate complex in the solid state; and such work is presented in this report. When an aqueous solution in the pH range 1–5.5 containing iron(III) chloride and two- to three-fold molar excess of sodium salicylate were allowed to stand in the dark a compound containing iron(III) and salicylate in the molar ratio 1:2 crystallized out. Electronic, infrared and Mössbauer spectral results, and magnetic moments data were used in characterizing these compounds.

EXPERIMENTAL

Preparation of Complexes

Complexes were prepared from solutions in the pH range 1–5.5 in increments of 0.5 pH unit. An aqueous solution of iron(III) chloride was prepared by dissolving 6.75 g (0.025 mole) $FeCl_3.6H_2O$ (BDH) in 100 ml water. To this solution was added an aqueous solution of sodium salicylate prepared by dissolving 12 g (0.075 mole) sodium salicylate (BDH) in about 100 ml water. The pH of the solution was then adjusted to the desired value using perchloric acid or a solution of sodium hydroxide, and subsequently filtered to remove any precipitate or solid matter.[7] The filtrate was cooled in a refrigerator[8] for about two days during which crystals of the complex were formed. The crystals were collected by filtration, washed with ice-cold water and dried at room temperature in a vacuum desiccator. The compounds prepared in the pH range 1–5 were all violet in colour and exhibited the following elemental analysis.[9]

Anal. Calcd. for $Na_2[Fe_2(C_7H_4O_3)_4(H_2O)_2]$: C, 45.5; H, 2.7; Fe, 15.1. Found: C, 45.6; H, 3.1; Fe, 14.8.

The compound prepared by the above procedure at pH 5.5 was brown in colour and gave the following elemental analysis.

Anal. Calcd. for $Na_4[Fe_2(C_7H_4O_3)_4(OH)_2]$: C, 43.0; H, 2.3; Fe, 14.3. Found: C, 42.5; H, 2.6; Fe, 14.1.

No compound was obtained in the solid form from solutions at pH 6.0 or higher.

Physical Measurements

Infrared spectra in the 4000–650 cm^{-1} region were obtained with Perkin–Elmer 137 spectrometer using Nujol mulls between potassium bromide plates. A Perkin–Elmer Model 180 spectrometer was employed for the region 700–200 cm^{-1}, using Nujol mulls and polyethylene windows. Electronic absorption spectra were measured on a Zeiss RPQ 20A spectrophotometer, and the reflectance spectra of solid samples were obtained with the help of RA 20 reflectance attachment. pH measurements were effected using a Corning Model 7 pH meter and a combination glass-calomel electrode (Beckman No. 39142 A8).

The Mössbauer spectra were recorded with a constant acceleration velocity transducer coupled to ^{57}Co in Cu matrix source (initial activity 25 mCi) in the standard transmission geometry. The velocity calibration was done with metallic iron as a standard. Cylindrical acrylic cells of cross-sectional area 2 cm^2 were used to contain the powdered samples. Liquid sample in the sample holder was cooled to the liquid nitrogen temperature by dipping it directly into the liquid nitrogen (cooling rate 450°/min) before introducing into the cell compartment. The liquid samples were prepared as follows. An aqueous solution (~ 20 ml) containing 1.35 g (0.005 mole) $FeCl_3.6H_2O$ was mixed with an aqueous solution (~ 20 ml) containing 1.60 g (0.01 mole) sodium salicylate. The pH of the mixture was then adjusted to the desired value between 1–6 by adding HCl or a solution of NaOH and subsequently made up to 50 ml and filtered to remove any solid matter.

Magnetic susceptibilities of the solid samples were determined by the Gouy method. Calibration standards were water and solid ammonium iron(II) sulphate. Measurements were made at room temperature (295°K) and liquid nitrogen temperature (77°K).

RESULTS AND DISCUSSION

All the nine compounds obtained from solutions in the pH range 1–5 showed identical elemental analysis results and agreed to the empirical formula $Na[Fe(C_7H_4O_3)_2H_2O]$ (this compound is denoted hereafter as *A*). The inclusion of coordinated water was in agreement with the infrared spectra[10,11] which showed strong bands at 795 cm^{-1} and 3300 cm^{-1}. These bands were absent in the ligand spectrum. The compound obtained from solution at pH 5.5 (hereafter referred to as *B*) lacked the band at 795 cm^{-1} while a new band appeared at 842 cm^{-1} which was also absent in the ligand spectrum. Since this band was typical of Fe–OH bending mode[12] an empirical formula $Na_2[Fe(C_7H_4O_3)_2OH]$, which was also in agreement with the elemental analysis results, was assigned to the compound *B*.

The compounds *A* as well as *B* exhibited strong infrared absorption bands at 885 cm^{-1}. This band corresponds to the asymmetric stretching frequency of an oxo-bridged Fe–O–Fe dimer.[13–15] This suggested that compounds *A* and *B* were dimeric with Fe–O–Fe bridge bonds. This conclusion was strongly

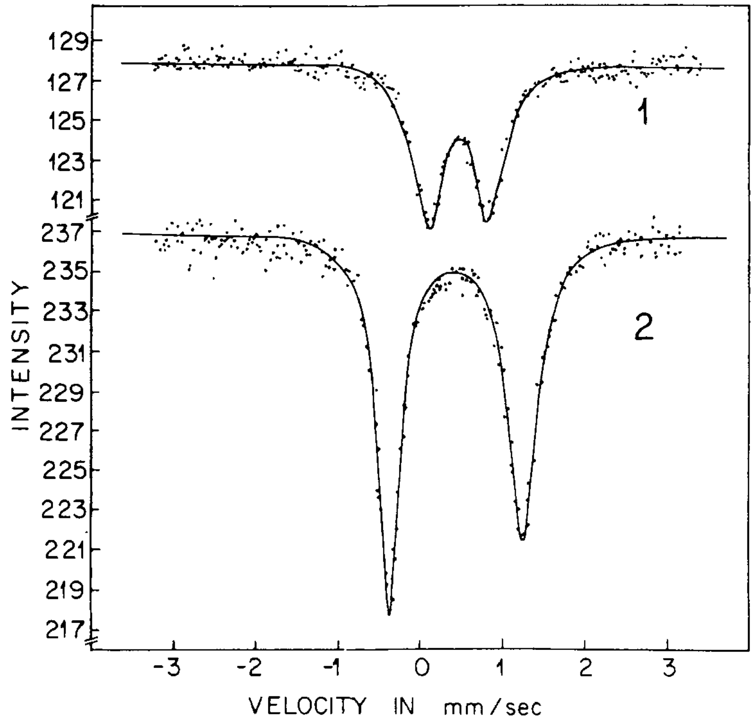

FIGURE 1 Mössbauer spectra of the frozen solution at pH 2.0 (spectrum 1), and the compound isolated from solution at pH 3.0 (spectrum 2). All compounds isolated from solutions in the pH range 1.0–5.5 exhibited spectra identical to 2. The velocity scale is with respect to natural iron.

supported by the Mössbauer spectral data (Figure 1). Compounds *A* and *B* exhibited identical isomer shift values (I.S. = 0.484 mm sec^{-1} with respect to natural iron) typical of a high-spin d^5 iron system,[16,17] while the quadrupole splitting value (Q.S. = 1.64 mm sec^{-1} for both *A* and *B*) was representative of compounds with Fe–O–Fe bridge bonds.[16,17]

The far-infrared spectra of compounds *A* and *B* exhibited three bands at 255, 340 and 415 cm^{-1} which were absent in the spectra of the ligands. A proper assignment of these bands is difficult. They probably arise from the Fe–O and Fe–O–Fe stretching vibrations of the bridge-bond. Since it is reasonable to expect the symmetric stretching vibration of Fe–O–Fe at lower frequency than Fe–O vibrations,[18] the band at 255 cm^{-1} may be assigned to the symmetric Fe–O–Fe vibration, while the other two bands to the Fe–O vibrations. At any case, attribution of one or more of these bands to vibrations of the Fe–O bond obtained by the coordination of phenolic or carboxylic oxygen (other than the bridge oxygen) to iron(III) may not be ruled out.

A comparison of the Mössbauer spectra of the frozen solution (Figure 1) with those of compounds *A* and *B* showed that the species in aqueous solution is mononuclear. The Mössbauer spectra of the frozen solutions were similar irrespective of their pH in the range 1.0–6.0 indicating that the Mössbauer parameters were uninfluenced by the number of salicylate per iron(III) ion. The isomer shift value for the frozen solutions (0.534 mm sec^{-1} with respect to natural iron) agreed reasonably well with those for compounds *A* and *B*, indicating a high-spin d^5 iron in all these compounds. But the quadrupole splitting value (0.726 mm sec^{-1}) is that expected for a mononuclear complex of low symmetry of the iron environment.[17] This shows that Fe–O–Fe bridge in non-existent in aqueous solutions of the complex obtained by mixing iron(III) salt and salicylate ion.

In addition to the absorptions of the salicylate ligands in the 300–200 nm region, the reflectance spectra of compound *A* showed a broad absorption in the 600–450 nm region with ϵ_{max} at 520 nm and two shoulders at 400 and 350 nm, while that of compound *B* exhibited three shoulders at 475, 400 and 350 nm. A comparison of the reflectance spectra of compounds *A* and *B* with an electronic absorption spectrum of a solution at pH 2.5 containing iron(III) and salicylate in the molar ratio 1:2, which exhibited an absorption band with ϵ_{max} at 520 nm and a shoulder at 325 nm, was made. The only significant difference was the appearance of the shoulder at 400 nm in the reflectance spectra of compounds *A* and *B* and its absence in the solution spectrum. Since the Mössbauer spectra clearly indicated the absence of Fe–O–Fe bridge in the solution of the complex and its presence in the compounds *A* and *B*, the shoulder at 400 nm may be attributed to the charge-transfer from the bridge-oxygen to iron(III).

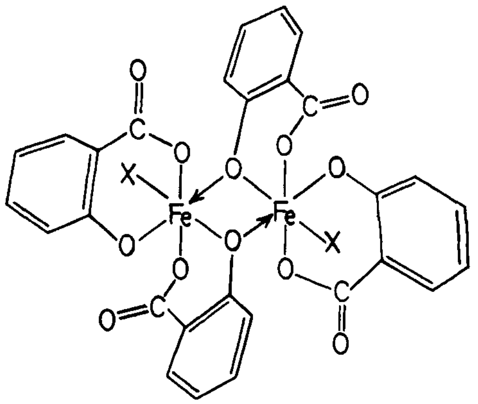

FIGURE 2 A probable structure for compound *A* or *B*. X represents H_2O and OH^-, respectively, in compounds *A* and *B*.

Normally iron(III) binuclear complexes containing linear Fe–O–Fe bridge show a magnetic moment of the order of 1.5 B.M. per iron(III) ion[13,19–23] due to the exchange interaction between the two d^5 iron(III) centers. But compounds *A* and *B* investigated in the present study showed magnetic moments normal to high-spin d^5 iron(III) complexes. Compounds of the *A* series gave the effective magnetic moments values 5.62 and 5.64 B.M. per iron(III) ion at 295° and 77°K, respectively, while for the compound *B* the effective magnetic moments were 5.32 and 5.47 B.M. per iron(III), respectively, at 295° and 77°K.[24] It is possible that these compounds contain bend Fe–O–Fe bonds, thus rendering the exchange interaction very weak or non-existent. At least one such case has been observed for the complex formed between iron(III) and N,N-ethylenebis(salicylideneiminato) ligand.[25] Since the phenolic oxygen or the carboxylate oxygen enter into the Fe–O–Fe bridge formation[26] in the compounds *A* and *B*, existence of a linear iron–oxygen–iron bridge is impossible. Hence, compounds *A* and *B* are considered to be binuclear with two bend Fe–O–Fe bridges. A possible structure for these compounds is presented in Figure 2.

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8. Crystallization occurs at room temperature also, but it takes longer time. Crystallization is comparatively faster in the pH range 1–3.
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