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Existence and Stability of a Simple Sulfide of Iron(III)

Sir:

The existence of a simple sulfide of iron(III) has been debated periodically for several years.¹⁻⁸ The central difficulties that have produced much of the debate are, first, the apparent instability of the compound and second, the lack of a good method for characterizing insoluble amorphous or microcrystalline materials of this type. In view of the possible geological significance of iron(III) sulfide⁹ and its relation⁷ to iron-sulfur minerals (pyrite, marcasite) that are a major

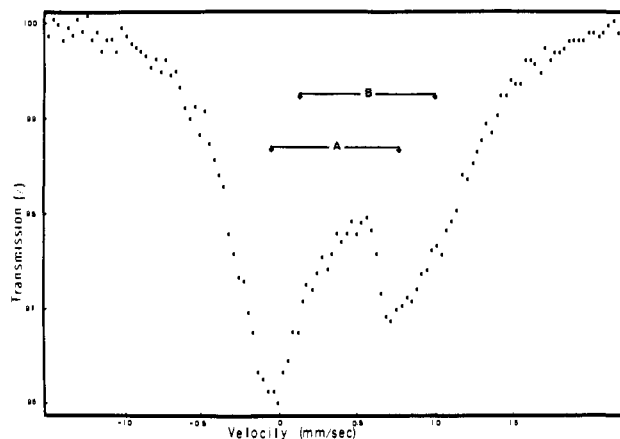


Figure 1. Mössbauer spectrum of iron(III) sulfide at 78 K (bar indicates error).

problem in the utilization of many coals, we have undertaken a detailed study of the chemical and physical properties of this material. We report here a synthesis, infrared characterization, and Mössbauer study with particular emphasis on the thermal stability of the compound. Previous reports^{4,5} on the synthesis of Fe_2S_3 have casually mentioned Mössbauer measurements, but details (center shifts, quadrupole splittings, thermal effects) were not given.

It is claimed that Fe_2S_3 can be obtained from iron(III) alkoxides and H_2S in organic solvents,⁴ from ammoniacal solutions of iron(III) tartrates and HS^- ion,⁴ from H_2S and $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ⁸ or suspensions of $\text{Fe}(\text{OH})_3$ at pH 9.5,⁵ and by titrating FeCl_3 with Na_2S .¹⁰ The first two methods give products that are heavily contaminated and, importantly, all previous preparations apparently were carried out at room temperature, or higher.

We have prepared¹¹ iron(III) sulfide in an amorphous form by treating stoichiometric quantities of aqueous Fe(III) with aqueous Na_2S at 0°C or below. Examination of the material with a scanning electron microscope equipped with an energy dispersive x-ray spectrometer confirmed the fact that sodium and chloride were not present and that the atomic ratio of Fe:S is 1:1.5. Thus at least on an empirical basis, the material prepared is Fe_2S_3 . The Mössbauer spectrum¹² of the compound at 78 K is shown in Figure 1; this spectrum is basically different from that of any of the known iron sulfides or compounds such as NaFeS_2 .⁶ The spectrum was analyzed by using a nonlinear least-square fitting program assuming Lorentzian line shapes. The best fit was obtained with two doublets with the following center shifts (CS) and quadrupole splittings (QS): doublet A, $\text{CS} = 0.35 \pm 0.06$ mm/s, $\Delta E_Q = 0.82 \pm 0.06$ mm/s; doublet B, $\text{CS} = 0.51 \pm 0.12$ mm/s, $\Delta E_Q = 0.88 \pm 0.12$ mm/s. These results indicate that there are two different environments for the iron ions in the compound, both with a symmetry lower than cubic. The observed CS is consistent with iron(III) or low-spin iron(II).¹³ In the latter case the ground state is non-magnetic, as in pyrite, FeS_2 .¹⁴

In order to characterize fully the charge state of the iron ion, Mössbauer measurements were carried out at 4.2 K. A six-line pattern with relatively broad line widths was obtained, as shown in Figure 2. The hyperfine magnetic field at the ^{57}Fe nucleus is 253 ± 6 kOe.¹⁵ The presence of a magnetic splitting at 4.2 K completely excludes the presence of iron(II), confirming the formation of the compound as a sulfide of iron(III). It is to be noted that the presence of a similar hyperfine magnetic field for the two sites of iron excludes the possibility of having two different compounds. The value observed for the splitting is much smaller than that expected for high-spin iron(III),¹⁶ indicating a high degree of covalency. In order to determine the type of order in this compound, measurements

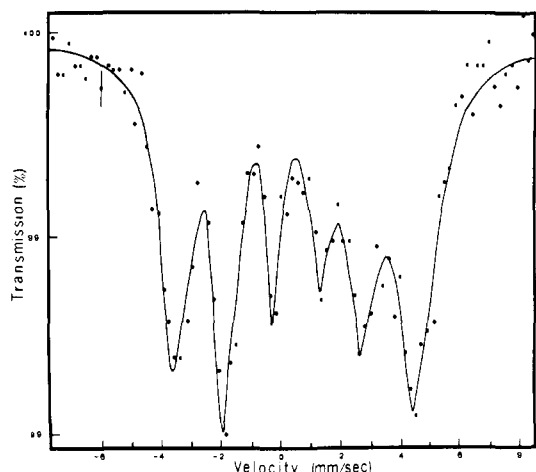


Figure 2. Mössbauer spectrum of iron(III) sulfide at 4.2 K (bar indicates error).

were carried out at 4.2 K with an external magnetic field applied collinear with the γ -ray direction. This resulted in a broadening of the outer Mössbauer lines, indicating the presence of magnetic moments at the iron ions aligned in opposite directions. Thus, it can be inferred that iron(III) sulfide is ordered antiferromagnetically at 4.2 K.

Mössbauer measurements at elevated temperature also have been made, the details of which will be published in future work. Suffice it to say here that an irreversible transformation to other products begins to occur at 20 °C in vacuo. Although the decomposition is slow considerable doubt is thus cast on the reliability of the previous synthetic procedures, all of which would appear to have been carried out at temperatures near that where Fe_2S_3 decomposes.

The infrared spectrum¹⁷ of iron(III) sulfide exhibits bands at 795 (sh), 485 (br), 390, and 320 cm^{-1} . The spectrum clearly is different from that of FeS_2 and other iron sulfide minerals.¹⁸

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- In a typical preparation 500 mL of 0.0483 M FeCl_3 was treated with 500 mL of 0.0737 M Na_2S at -2 °C under an atmosphere of N_2 . The black air-sensitive precipitate that formed was permitted to settle and then was filtered (with extreme difficulty). The product was washed with ice water until the filtrate gave a negative test for chloride, and it then was washed with cold 25:75 $\text{CH}_3\text{OH}:\text{H}_2\text{O}$. The filtrate contained no detectable iron(III), iron(II), or S^{2-} . After the temperature of the gelatinous precipitate was reduced to ca. -5 °C, the sample was placed over P_4O_{10} in an evacuated chamber and pumped, the temperature remaining at -5 °C until the precipitate turned to a black, dry powder (~ 4 weeks). The last traces of water are difficult to remove, and the compound may contain water of hydration. A portion of the powder was decomposed with nitric acid at room temperature. The resulting solution gave negative tests for Na^+ and Cl^- .
- Mössbauer measurements were made using a $^{57}\text{Co}:\text{Pd}$ source with an initial activity of 25 mCi. The spectrometer was calibrated with standard iron foils, and the center shift values reported are with respect to metallic iron.
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Carbon-Carbon Bond Formation at C_4' of a Nucleoside. Synthesis and Utilization of a Uridine 4',5'-Enamine¹

Sir:

The search for methods allowing substituent incorporation at C_4' of nucleosides began with the isolation and structure identification of nucleocidin (**1**), a powerful, but toxic, anti-trypanosomal agent with a fluorine in this unique position on the carbohydrate ring.²⁻⁵ Synthetic methods have thus far been developed which allow incorporation of fluorine,⁶⁻⁸ various alkoxyl groups,^{1,9-11} and hydroxymethyl.¹²⁻¹⁴ The challenge of devising a reasonably versatile method for carbon-carbon bond formation at C_4' , however, is still at hand. We wish to report that alkylation of a nucleoside 4',5'-enamine with allylic halides provides a solution to this problem.

Our work in the area of nucleoside 4',5'-enol acetates¹⁵ and their conversion to certain 4'-substituted compounds¹ prompted us to examine the feasibility of utilizing a 4',5'-enamine as a vehicle for introduction of a carbon-carbon bond via enamine alkylation. To date no literature reports exist for the formation of a nucleoside enamine, although recently a carbohydrate enamine was reported.¹⁶ Treatment of 2',3'-

