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Note

# About the synthesis of the prismane [NEt<sub>4</sub>]<sub>2</sub>[Fe<sub>6</sub>S<sub>6</sub>I<sub>6</sub>]

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## Abstract

In the literature there are conflicting views as to whether the iron–sulfur prismane  $[NEt_4]_2[Fe_6S_6I_6]$  can be prepared in a one-pot synthesis from iron, sulfur, iodine and tetraethylammonium iodide. The cluster can be prepared in this way, provided the work-up conditions are rigorously controlled. The spectroscopic properties of  $[NEt_4]_2[Fe_6S_6I_6]$  prepared in a one-pot synthesis are compared with those of a sample prepared by the oxidative transformation of  $[NEt_4]_2[Fe_4S_4I_4]$  and to those of other iodo–iron–sulfur clusters.  $\bigcirc$  1999 Elsevier Science S.A. All rights reserved.

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# 1. Introduction

An extensive literature exists on the synthesis of ironsulfur clusters [1-4]. In 1984 Pohl and coworkers. reported the synthesis of the prismane cluster anion  $[Fe_6S_6I_6]^{2-}$ , according to Eq. (1), isolated as the tetraethylammonium salt [5,6]. It was suggested that the formation of the cluster is via lower-charged species, which were readily soluble in dichloromethane but which have never been isolated. Also, dependent on the molar ratios of the reactants, other iodoiron-sulfur clusters should be accessible by the same route. However, Coucouvanis et al. were unable to repeat the reported synthesis and suspected that  $[Fe_6S_6I_6]^{2-}$  was only a minor byproduct since they obtained [FeI<sub>4</sub>]<sup>-</sup> in excellent yield. They also reported a general procedure for the synthesis of  $[Fe_6S_6X_6]^{2-}$  (X = Cl, Br) anions based on the oxidation of  $[Fe_4S_4X_4]^{2-}$  clusters in dichloromethane [7] (Eq. (2)). Moreover, the same authors reported that solutions of the prismane dianions in polar solvents (MeCN, DMF) are unstable. The transformation of  $[Fe_6S_6X_6]^{2-}$  to  $[Fe_4S_4X_4]^{2-}$ clusters and unidentified byproducts is evident in the observed changes in the electronic spectra. In the presence of excess X<sup>-</sup> the transformation occurs quantitatively [7] according to Eq. (3). The same transformation occurs for the iodo-prismane [8].

$$6Fe + 6S + 2I_2 + 2I^- \rightarrow [Fe_6S_6I_6]^{2-}$$
 (1)

$$B[Fe_4S_4X_4]^{2-} + 2[Fe(C_5H_5)_2]^+ \rightarrow 2[Fe_6S_6X_6]^{2-} + 2Fe(C_5H_5)_2$$
(2)

$$[Fe_6S_6X_6]^{2-} + 2X^- \to [Fe_4S_4X_4]^{2-} + [Fe_2S_2X_4]^{2-}$$
(3)

In this paper we report the synthesis of  $[NEt_4]_2[Fe_6S_6I_6]$  by an adaptation of the Coucouvanis method and show that the same material can be obtained by the method of Pohl [5,6,8] if the work-up conditions are controlled.

## 2. Experimental

All operations were performed under dinitrogen and solvents were dried as appropriate before use. The materials  $[NEt_4]_2[Fe_2S_2I_4]$  [9],  $[NEt_4]_2[Fe_4S_4I_4]$  [9],  $[NEt_4]_3[Fe_6S_6I_6]$ [10] and  $[Fe(C_5H_5)_2][FeCl_4]$  [11] were prepared by published procedures. Mössbauer spectra were recorded on an ES-Technology MS105 spectrometer at 77 K, using a 925 MBq <sup>57</sup>Co source in a rhodium matrix, and were referenced against iron foil at 298 K. All measurements were at zero field on samples in the solid state. Variable temperature magnetic susceptibility measurements were made on polycrystalline samples in a field of 0.1 T using a Quantum Design SQUID magnetometer. The susceptometer was calibrated with (NH<sub>4</sub>)<sub>2</sub>Mn(SO<sub>4</sub>)<sub>2</sub>.12H<sub>2</sub>O. Correction for diamagnetism was estimated from Pascal constants as  $-700 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ . UV-Vis spectra and infrared spectra were recorded on a Hitachi 2000V and Perkin-Elmer 16F PC FT-IR spectrophotometer, respectively.

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Low frequency infrared absorbance (cm <sup>-1</sup> ) <sup>a</sup> for $[NEt_4]_2[Fe_6S_6I_6]$ (1) and other iodo-iron-sulfur clusters											
$[NEt_4]_2[Fe_6S_6I_6]$ (I)	466	452			394		292		238	225	
$[NEt_4]_2[Fe_2S_2I_4]$	466	452	432	415		322		263		228	220
$[NEt_4]_2[Fe_4S_4I_4]$	466	452	420		382	344	288				

<sup>a</sup> As Nujol mulls between polyethylene discs.

Table 1

# 2.1. Preparation of $[NEt_4]_2[Fe_6S_6I_6]$ (I) by oxidative transformation

 $[NEt_4]_2[Fe_2S_2I_4]$  (0.166 g, 14.84 mmol) and  $[Fe(C_5H_5)_2]$ -[FeCl<sub>4</sub>] (0.038 g, 0.099 mmol) were stirred together in dichloromethane (40 ml) for 4 h. The volume of the solvent was reduced in vacuo to 20 ml and diethyl ether (20 ml) added. After storage at 253 K for 2 days a black solid was collected by filtration and washed with diethyl ether. Yield 65%.

# 2.2. Preparation of $[NEt_4]_2[Fe_6S_6I_6]$ (I) by one-pot synthesis and of mixtures II-VI

All syntheses followed the same initial procedure. A mixture of iron (0.84 g, 15 mmol), sulfur (0.48 g, 15 mmol), iodine (1.27 g, 5 mmol) and tetraethylammonium iodide (1.29 g, 5 mmol) in tetrahydrofuran (100 ml) was refluxed for 48 h. The resultant solution was filtered hot. The product mixtures were isolated using the following procedures:

- I. The filtrate was concentrated in vacuo to 15 ml then dichloromethane (25 ml) was added, after 2 days at 253 K a black solid was obtained or the filtrate was concentrated in vacuo to 15 ml, dichloromethane (15 ml) was added, after standing overnight at 253 K a black solid was isolated.
- II. The filtrate was taken to dryness and to the residue was added dichloromethane (25 ml). After 3 days at 253 K a black solid was isolated.
- III. The filtrate was evaporated to dryness in vacuo and the residue was isolated as a black solid.
- IV. The filtrate was concentrated in vacuo to 10 ml, dichloromethane (15 ml) was added, the mixture stirred for 2 h then, after 2 days at 253 K, a black solid was collected.
- V. The filtrate from the isolation of I was allowed to stand for several days and further black solid was collected.
- VI. To product mixture II MeCN (20 ml) was added, the mixture was filtered and the filtrate concentrated in vacuo to 10 ml, diethyl ether (5 ml) was added and a black solid was obtained.

# 3. Results and discussion

The  $[NEt_4]_2[Fe_6S_6I_6]$  (I) prismane cluster can be prepared by the oxidative transformation of  $[Fe_4S_4I_4]^{2-}$  following

Table 2							
Mössbauer	parameters <sup>a</sup> in	1 the	solid	state	and	zero	field

	<i>T</i> (K)	i.s.	q.s.	hwhm <sup>b</sup>
$[NEt_4]_2[Fe_6S_6I_6]$ (I)	77	0.49	1.03	0.16 <sup>c</sup>
		0.49	0.64	0.23 <sup>c</sup>
	185	0.43	0.66	0.26
	298	0.37	0.67	0.24
$[NEt_4]_2[Fe_2S_2I_4]$	77	0.36	1.04	0.12
$[NEt_4]_2[Fe_4S_4I_4]$	77	0.48	0.90	0.21
$[NEt_4]_3[Fe_6S_6I_6]$	77	0.51	1.06	0.13
[NEt <sub>4</sub> ][FeI <sub>4</sub> ]	77	0.42	0.00	0.15

<sup>a</sup> mms<sup> $\pm 1$ </sup>,  $\pm \le 0.01$ .

<sup>b</sup> hwhm = half width at half maxima.

<sup>c</sup> Ratio 1:2

the method of preparation for the analogous chloro- and bromo-derivatives [7]. Cluster I is stable to 510 K under an atmosphere of dinitrogen and decomposes slowly in air at room temperature. It is soluble in acetonitrile, dimethylsulfoxide and dimethylformamide, and sparingly soluble in tetrahydrofuran and dichloromethane, but insoluble in diethyl ether. An acetonitrile or dichloromethane solution of the cluster shows a major UV-Vis absorbance at 360 nm consistent with those of  $[Fe_6S_6X_6]^{2-}$  (in dichloromethane): X = Cl, 287 nm; X = Br, 326 nm, and a minor peak at 702 nm. The infrared spectrum is different to that of  $[NEt_4]_2[Fe_4S_4I_4]$  and  $[NEt_4]_2[Fe_2S_2I_4]$  (Table 1).

The Mössbauer spectral parameters at three temperatures are collected in Table 2. At 298 and 185 K, a single quadrupole split doublet is observed. The isomer shift (i.s.) and quadrupole splitting (q.s.) values are similar to those observed for  $[Fe_6S_6Cl_6]^{2-}$  (i.s. = 0.39, q.s. = 0.66 mms<sup>-1</sup>, at 200 K) [12] and  $[Fe_6S_6Br_6]^{2-}$  (i.s. = 0.44, q.s. = 0.70 mms<sup>-1</sup>, averaged values above 100 K) [13]. Previously, it was demonstrated that, on cooling  $[Fe_6S_6X_6]^{2-1}$ below 50 K, the Mössbauer spectrum resolves into three overlapping doublets. This reversible effect was associated with a structural distortion at the lower temperatures, giving three chemically distinct iron sites [13]. Kröckel et al. [14] have expanded this explanation in terms of temperaturedependent valence delocalisation. At the lowest temperatures two iron atoms can be considered to be in the oxidation state +3, two in the oxidation state +2, and two in between. At higher temperatures (above 150 K), when a single Mössbauer doublet is observed, all six iron atoms appear equivalent with an oxidation state of +2.67. For [NEt<sub>4</sub>]<sub>2</sub>- $[Fe_6S_6I_6]$  we observe the beginnings of this resolution at 77 K, the spectrum at this temperature being best fitted by

two overlapping doublets of intensities of 1:2. The change from a two-quadrupole split doublet to a one-quadrupole split doublet spectrum with temperature is fully reversible. The Mössbauer parameters are different to those measured for  $[NEt_4]_2[Fe_2S_2I_4]$ ,  $[NEt_4]_2[Fe_4S_4I_4]$  and the reduced prismane  $[NEt_4]_3[Fe_6S_6I_6]$ , Table 2.

The room temperature effective magnetic moment for **I** is 7.2 BM, a value lower than that expected for two iron(II)- and four iron(III)-isolated high spin tetrahedral iron atoms. When cooled, the effective magnetic moment decreases to 2.5 BM at 2 K. These features indicate that an intramolecular antiferromagnetic interaction occurs in prismane **I**. The magnetic moment for the chloro-anologue,  $[NEt_4]_2[Fe_6S_6Cl_6]$ , at room temperature, was estimated to be 3.1 BM by NMR measurements in solution [7], a value much lower than that of **I**. It is known that structural distortions and the nature of the peripheric ligands can significantly affect the magnitude of the magnetic coupling [15] and the observed difference can be attributed to such effects.

We have repeated the synthetic procedure of Pohl and by variation of work-up conditions (see Section 2) can prepare, reproducibly, either  $[NEt_4]_2[Fe_6S_6I_6]$  (I) or various product mixtures II–IV, summarised in Scheme 1. Cluster I was precipitated as a black solid, 40% yield, by addition of dichloromethane to the tetrahydrofuran reaction solution after concentration. The infrared (Table 1), Mössbauer (Table 2), and UV–Vis spectra are equivalent to those of I prepared by the alternative route. The reversible dependence of the variation of Mössbauer complexity with temperature was again observed. There was no evidence of contamination by  $[NEt_4][FeI_4]$ . The infrared absorbance at 238 cm<sup>-1</sup> is common to the prismane and  $[NEt_4]$ .

 $[FeI_4]$  [16]. Under these preparative conditions the  $[NEt_4]_2[Fe_6S_6I_6]$  prismane can be prepared by the one-pot synthesis.

The following preparative methods led to product mixtures (Scheme 1) as detected by Mössbauer and infrared spectroscopy. If the reaction mixture is taken to dryness before adding dichloromethane, as previously reported [5,6], then a mixture of prismane and  $[NEt_4][FeI_4]$  is obtained II. By Mössbauer spectroscopy, assuming an equivalent recoil-free fraction for each type of iron atom, then the mixture composition is approximately two tetraiodoferrite to one prismane. Product mixture III, obtained when tetrahydrofuran solvent is completely removed, has the same composition. This helps to explain the difficulties of others [7] to reproduce the published preparation. When tetrahydrofuran is removed to a small volume prior to the addition of a smaller volume of dichloromethane than used in the isolation of **I**, and the mixture is stirred for 2 h before standing for 2 days, then a mixture of [NEt<sub>4</sub>]<sub>2</sub>[Fe<sub>2</sub>S<sub>2</sub>I<sub>4</sub>] and  $[NEt_4][FeI_4]$  is obtained IV. A similar mixture V is obtained from the filtrate obtained after collection of **I**, if it is allowed to stand for several days. On recrystallisation of mixture II from MeCN/Et<sub>2</sub>O, [NEt<sub>4</sub>]<sub>2</sub>[Fe<sub>2</sub>S<sub>2</sub>I<sub>4</sub>] is obtained as the only product VI.

To conclude, the prismane  $[NEt_4]_2[Fe_6S_6I_6]$  can be obtained by a one-pot synthesis provided the work-up conditions are rigorously controlled. We have shown that if care is not taken various mixtures can easily form. The ease with which such clusters as those described above can be readily formed from elemental iron, sulfur and iodine with iodide, may support the suggestion that such metal– sulfur clusters could have formed during the very early stages of evolution [17,18].



Scheme 1. (a) Oxidative transformation; (b) conc. +  $CH_2Cl_2$ , 2 days, collect; (c) conc. +  $CH_2Cl_2$ , overnight, collect; (d) to dryness +  $CH_2Cl_2$ , 3 days, collect; (e) to dryness; (f) conc. +  $CH_2Cl_2$ , stir 2 h, 2 days, collect; (g) filtrate after collection of **I**, several days, collect; (h) **II** +  $CH_3CN$ , conc. +  $Et_2O$ , collect.

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