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A Mössbauer Spectroscopic Investigation of the Iron Sulphido–Carbonyl Clusters $[Fe_2(\mu_2\text{-}S)_2(CO)_6]$, $[Fe_3(\mu_3\text{-}S)_2(CO)_9]$ and the 1:1 Adduct $[Fe_2(\mu_2\text{-}S)_2(CO)_6]\cdot[Fe_3(\mu_3\text{-}S)_2(CO)_9]$

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Abstract

The 1:1 adduct '$[Fe_2(\mu_2\text{-}S)_2(CO)_6][Fe_3(\mu_3\text{-}S)_2(CO)_9]$' (**I**) shows ^{57}Fe Mössbauer parameters clearly different to those of the parent $[Fe_2(\mu_2\text{-}S)_2(CO)_6]$ (**II**) and $[Fe_3(\mu_3\text{-}S)_2(CO)_9]$ (**III**) species. This indicates that the electronic environments of the iron atoms are significantly modified on adduct formation. The trinuclear complex (**III**) shows equivalent electronic environments for the iron atoms, although two iron atoms are crystallographically quite distinct from the third.

Introduction

The search for viable models for the iron–molybdenum co-factor of nitrogenase has led to considerable interest in the synthesis and properties of iron sulphido clusters. The dimer $[Fe_2(\mu_2\text{-}S)_2(CO)_6]$ (**II**) has proved to be a convenient precursor for the synthesis of mixed-metal–sulphido clusters. However, the complex is not easy to prepare pure in high yield as the literature synthesis leads to a mixture of **II** and the trimer **III**. Fractional sublimation produces a low yield of **II** but further sublima-

TABLE I. ^{57}Fe Mössbauer Spectroscopic Parameters

Complex	Temperature (K)	δ (mm s^{-1})	Δ (mm s^{-1})	Γ^a (mm s^{-1})	Absorption area (%)	Fit^b
$[Fe_2(\mu_2\text{-}S)_2(CO)_6]$ (II)	298	0.008(6)	1.088(10)	0.144(8)	100(6.5)	
	78	0.068(4)	1.088(7)	0.139(6)	100(5.0)	
	4.2^c	0.08	1.11	–	–	
$[Fe_3(\mu_3\text{-}S)_2(CO)_9]$ (III)	298	−0.028(2)	0.548(4)	0.139(3)	100(2.6)	
	78	−0.040(2)	0.543(2)	0.143(2)	100(1.7)	
$[Fe_2S_2(CO)_6][Fe_3S_2(CO)_9]$ (I)	298	0.000	1.087	0.141(21)	23.3(4.0)	(i)
		−0.028	0.543	0.186(9)	76.7(4.6)	
	78	0.068	1.087	0.199(10)	46.4(2.8)	(i)
		−0.040	0.540	0.202(9)	53.6(2.8)	
	298	−0.023(14)	1.020(54)	0.142(40)	23.7(9.5)	(ii)
		−0.020(7)	0.554(38)	0.191(18)	76.3(10.1)	
	78	0.081(2)	1.036(7)	0.161(4)	41.1(1.6)	(ii)
		0.055(2)	0.574(7)	0.185(3)	58.9(1.7)	
	298	0.000	1.087	0.122(31)	14.9(4.9)	(iii)
		−0.018(7)	0.588(20)	0.202(14)	85.1(6.5)	
	78	0.068	1.087	0.142(4)	30.1(1.0)	(iii)
		0.055(2)	0.613(4)	0.196(3)	69.8(1.2)	
	298	−0.026(12)	1.006(29)	0.148(24)	26.8(5.0)	(iv)
		−0.028	0.543	0.187(10)	73.1(5.4)	
	78	0.083(3)	0.817(5)	0.242(4)	86.5(2.09)	(iv)
		−0.040	0.540	0.159(15)	13.5(1.75)	

Values in parentheses are standard deviations. Where none given parameters were held. ^{a}Half width at half height. ^{b}For details of fit see explanation in text. ^{c}Data from ref. 4.

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tion at higher temperature gives only a crystalline 1:1 adduct without further separation. This stability of the 1:1 adduct is surprising as its crystal structure [1] suggests that **II** and **III** are little changed from their uncombined individual structures [2, 3]. In view of the Fe–C and C–O bond lengths found in the structure of the dimer component of the adduct, any detailed discussion of structural changes occurring on formation of the adduct is inappropriate. However, Mössbauer spectroscopy provides the opportunity to establish if the electronic environments of the iron atoms change on adduct formation. We have accordingly undertaken a detailed Mössbauer investigation of both complexes **II** and **III** and their 1:1 adduct **I**.

Results and Discussion

Data Collection

The Mössbauer parameters for all three complexes are summarised in Table I. A recent publication [4] presents parameters for complex **II** at 4.2 K in total agreement with our result. The spectrum of complex **III** has been measured [5] over a temperature range from 80 K upwards; at comparable temperatures the quadrupole splittings agree. The parameters for the mixed compound **I** were computer fitted in four different ways: (i) both sites held to the parameters found in complexes **II** and **III**, but with linewidths and intensities allowed to vary, (ii) both sites allowed to vary to best fit, (iii) one site held to parameters for **II** with linewidth and intensity allowed to vary; the other allowed to vary to best fit, (iv) one site held to parameters for **III** with linewidth and intensity allowed to vary; the other allowed to vary to best fit.

From Table I (and Figs. 1 and 2) it can be seen that the optimum fit is realised by procedure (ii) (Fig. 1) and the worst for procedure (i). The parameters derived from fitting procedure (ii) indicate clearly that the environments of the iron atoms in the adduct **I** are quite distinct from those in either of the components **II** and **III**.

Additional evidence for the optimum nature of procedure (ii) comes from the linewidths it produces, which are significantly smaller than at least one site found by the other procedures. Moreover, the absorption areas for **I** at 78 K are consistent with the 1:1

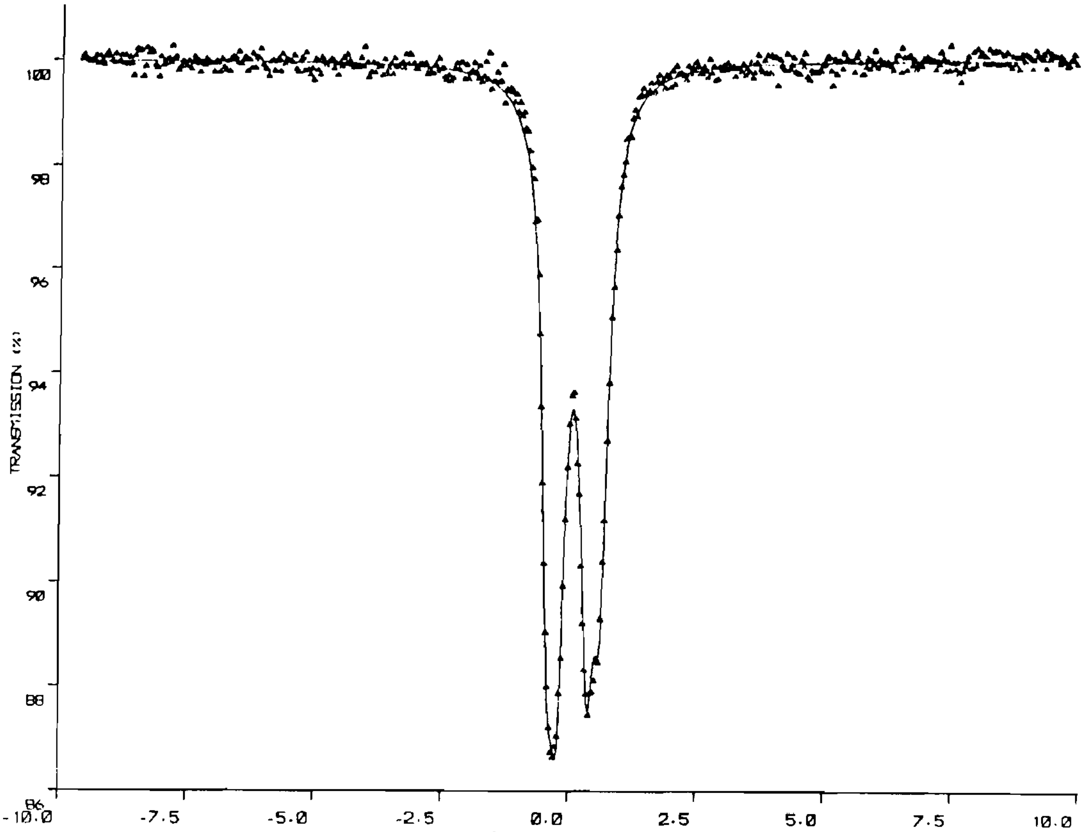

Fig. 1. ^{57}Fe Mössbauer spectrum (obtained at 78 K) of the mixed compound [$Fe_2(\mu_2\text{-}S)_2(CO)_6$][$Fe(\mu_3\text{-}S)_2(CO)_9$] (**I**) fitted by allowing the two doublets from **II** and **III** both to vary to the best possible fit (ii).

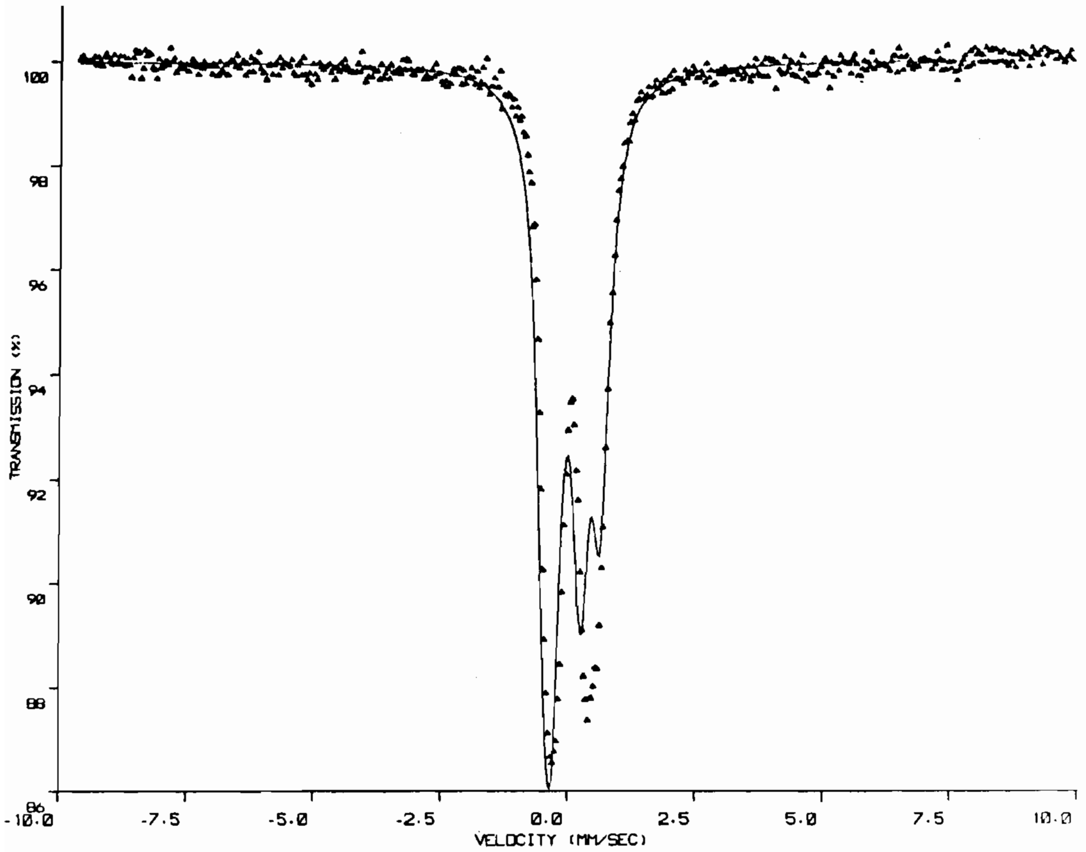

Fig. 2. ^{57}Fe Mössbauer spectrum as in Fig. 1 but holding both doublets from II and III to the data obtained for complexes II and III (see text fit (i)).

stoichiometry of **I**. The other procedures did not give the appropriate area ratios.

Results

The absorption area ratios for adduct **I** are significantly temperature dependent when using the variable fitting procedure (ii). At 78 K the ratio of 2:3 expected from the molecular formula is found and at this temperature the recoil free fractions of the different iron atoms would be expected to be similar. However, at room temperature this ratio is 1:3. This suggests that the recoil free fractions of the two parent molecules **II** and **III** are different at room temperature and that within the adduct the iron atoms [$Fe_3(\mu_3\text{-}S)_2(CO)_9$] are held more rigidly in the lattice than those of [$Fe_2(\mu_2\text{-}S)_2(CO)_6$)]. This is in agreement with the larger isotropic thermal parameters observed in the structure of the dimer component of the adduct, indicating that it has a freer thermal motion.

The largest other differences found in the Mössbauer data are for the quadrupole splittings of the [$Fe_2(\mu_2\text{-}S)_2(CO)_6$] molecules in the free state and in the adduct. The parameters for the trimer change comparatively little on adduct formation. This confirms that only for the dimer does combination of the dimer (**II**) and trimer (**III**) to form the adduct (**I**) cause significant modification of the electronic environment of the iron atoms.

This information coupled with the recoil fraction and X-ray data suggests that the somewhat flexible dimer is distorted via solid state interactions in the adduct. The relatively rigid trimer unit remains comparatively unperturbed in the adduct lattice.

A further point of interest is the apparently simple doublet observed for the three iron atoms of the trimer (**III**) although one iron is quite crystallographically distinct from the other two. The Mössbauer spectra indicate that the iron atoms experience very similar electronic environments (Fig. 3). This apparent contradiction might be attributed to the crystallographically distinct irons having coincidental identical electronic environments. However, a more probable interpretation is that although the Fe–Fe distances are 2.609, 2.582 and 3.371(10) Å the irons experience virtually identical electronic surroundings on the Mössbauer time scale. Similar simple spectra have been reported for other iron carbonyl clusters such as [$Fe_3(CO)_{11}]^{2-}$ [6] and $Fe_4(CO)_{13}]^{2-}$ [6, 7], though those of the triangles [$Fe_3(CO)_{12}$] [6, 8, 9]

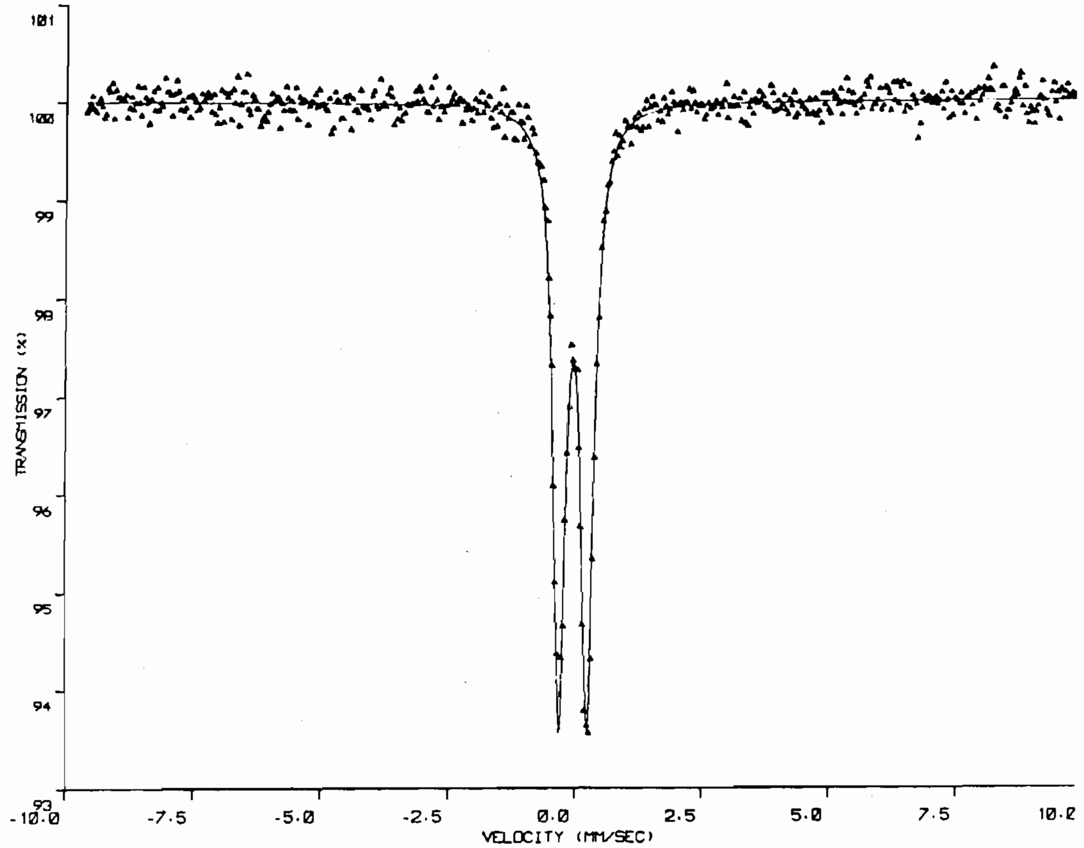

Fig. 3. ^{57}Fe Mössbauer spectrum (obtained at 78 K) of $[Fe_3(\mu_3\text{-}S)_2(CO)_9]$ (**III**).

and $[Fe_3(CO)_{11}H]^-$ [6, 10] show two distinct iron sites at 78 K. The iron atoms in the trimer (**III**) remain equivalent in the Mössbauer spectra even at low temperature.

Experimental

The Mössbauer spectra of the powders were recorded in aluminium holders on a constant acceleration spectrometer previously described [11]. The source was ≈25 mCi of ^{57}Co in Rh (obtained from the Radiochemical Centre, Amersham) at 20 °C. The source was moved with a saw tooth wave form, and the spectra were computer fitted. The velocity was calibrated and linearity of the waveform monitored by reference spectra of 10 mg cm^{-2} iron foil to which isomer shifts are referred. All spectra were recorded twice.

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