Effects of Temperature and Pressure on the Mössbauer Spectra of Models for the $[4Fe\text{-}4S]^{2+}$ Clusters of Iron−Sulfur Proteins and the Structure of $[PPh_4]_2[Fe_4S_4(SCH_2CO_2C_2H_5)_4]$

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Changes in the Mössbauer spectra of $[Cat]_2[Fe_4S_4(S^tBu)_4]$ salts where Cat = $N(alkyl)_4$ and PPh_4 are apparent when these compounds are subjected to temperature changes in the range 78−298 K or to pressures up to 6.28 GPa. The Mössbauer data are discussed in terms of the temperature and pressure dependence. It is revealed for the $[4Fe\text{-}4S]^{2+}$ clusters that the iron atoms become less electronically symmetric as the temperature is lowered or pressure is increased. The crystal structure of $[PPh_4]_2[Fe_4S_4(SCH_2CO_2C_2H_5)_4]$ is reported and discussed in relation to the effect of pressure on the Mössbauer spectroscopic data. It is possible to arrange the compounds into three classes depending on their response to the application of pressure.

Introduction

Naturally occurring $[4Fe\text{-}4S]^{2+}$ clusters are bound within large protein structures that are believed to control the redox potential and chemistry of the clusters.[1] It has been suggested that such control could be modeled by the interplay of cationic and anionic charges near the clusters.[2−5] Indeed, model compounds of the general formula $[NR_4]_2[Fe_4S_4(S^tBu)_4]$, where R = alkyl, were shown to have Mössbauer quadrupole splitting (ΔE_Q) values related to cation size[3−5] and hence presumably to anion−cation distance.[4] ΔE_Q arises from asymmetry in the electric field gradient around the iron atoms and can be considered to be a combination of two terms, q_{val} and q_{latt}, where q_{val} is the field gradient generated by the valence electrons and q_{latt} is the field gradient generated by all other charges in the lattice. q_{val} is positive, but usually q_{latt} is small and negative; however, in the model compounds, small cations gave q_{latt} contributions that were sufficiently negative to reduce ΔE_Q significantly.[2−5]

One way of examining the effect of changing the anion−cation distance on the Mössbauer parameters is to subject the lattice to changes in pressure. From previous experience,[4] it is expected that ΔE_Q would decrease as pressure increases because the anions and cations are squeezed closer together, thereby increasing the negative lattice effect (q_{latt}). The approach was particularly attractive, as the conformation of a protein could effectively exert compression effects on included clusters by moving charges or partially charged groups closer to the clusters. It should be stated that pressure changes in a diamond anvil cell (DAC) are applied isotropically but of course compression effects due to protein reorganization may exert electric field gradients that are not cubic.

When the lattice in a model compound is squeezed, not only might the cation approach closer to the core anion, but the cluster itself may be compressed. Using a range of cations, the lattice effect should thus be open to investigation. The work is at present somewhat restricted, as it was feasible to study such Mössbauer spectra under pressure only at room temperature with currently available facilities. The compounds chosen are of the general formula $[Cat]_2[Fe_4S_4(S^tBu)_4]$ where $[Cat]^+ = [NMe_4]^+$ (**1**), $[NEt_4]^+$ (**2**), $[NPr_4]^+$ (**3**), $[NPen_4]^+$ (**4**), and $[PPh_4]^+$ (**5**). Of these complexes, **1**, **2**, and **4** have been structurally characterized[4−6] and **3** has been shown to be isomorphous with the first two. Compound **1** was chosen, as it has a large q_{latt} at 78 K.[3−5] Along with these results, the structure and high-pressure Mössbauer spectroscopic data for $[PPh_4]_2[Fe_4S_4(SCH_2CO_2C_2H_5)_4]$ (**6**) are reported, discussed, and compared with those of **5**.

Experimental Section

Mössbauer spectra were recorded using previously reported methods at atmospheric[7] and high pressure.[8] Hydrostatic pressure was maintained in the DAC using a 1:1 mixture of pentane to isopentane. The DAC

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Table 1. Crystal Structure Data for Some of the Samples in the Study and a Relevant Additional Complex[a]

sample	Fe−Fe (Å)	Fe−S (Å)	Fe−L (Å)	S−Fe−S (deg)	Fe−S−Fe (deg)	*T* (K)	ref
1	2.741(3)	2.300(4)	2.261(4)	104.1(1)	73.6(1)	298	4
2[b]	2.759(8)	2.287(8)	2.254(3)	104.0	74.0	295	6
4	2.784(9)	2.296(22)	2.250(14)	103.4(7)	74.7(7)	298	4
$[Me_3NCH_2Ph]_2[Fe_4S_4(S^tBu)_4]$	2.753(5)	2.294(5)	2.261(6)	104.0(3)	73.9(3)	295	6
6	2.757(8)	2.285(5)	2.259(3)	103.8(2)	74.2(2)	298	this work

[a] Error ±0.02. [b] Mean and error taken from ref 6.

pressure was calculated using the ruby fluorescence method.[9,10] All spectra are referenced to a 25 μm natural iron foil at 293 K (high pressure) or 298 K (atmospheric pressure).

Mössbauer data at 78 K and ^1H NMR spectra showed no resonances other than those expected for the clusters and were in agreement with those seen previously.[4,5] ^1H NMR spectra were recorded on a JEOL GSX270 spectrometer in dmso-d_6 solution. Compounds **1**−**5** were prepared by adaptation of a standard procedure.[11] Compound **6,** $[PPh_4]_2[Fe_4S_4(SCH_2CO_2C_2H_5)_4]$, was prepared by an adaptation of the published procedure.[12] Under an atmosphere of dinitrogen, salt **5** (0.69 g, 0.5 mmol) was dissolved in dry, degassed MeCN (50 cm^3). $HSCH_2CO_2C_2H_5$ (0.3 g, 25 mmol) was added dropwise from a syringe. The mixture was stirred at room temperature for 20 min and the volume then reduced to ca. 10 cm^3. On addition of methanol (40 cm^3), a small amount of green precipitate formed, which was removed by filtration, and the volume of the filtrate was reduced to ca. 10 cm^3. Ethyl acetate (40 cm^3) was added and the mixture stored overnight at 253 K. The black crystals that formed were collected by filtration and washed with diethyl ether. A second crop of crystals was obtained after reduction of the volume to 25 cm^3, addition of diethyl ether (25 cm^3), and storage overnight at 253 K (0.44 g, 56%). ν_{max}: 1728 cm^{-1} (CO) (Nujol). δ_H (dmso-d_6): 13.16 (SCH_2), 7.87 (PPh_4), 4.13 (CO_2CH_2), 1.24 (CH_3).

A crystal was placed inside a Lindemann glass capillary, which was then mounted on an Enraf-Nonius CAD-4 diffractometer,[13,14] and Mo Kα ($\lambda = 0.710\ 73$ Å) radiation was used for data collection. A primitive unit cell was used and later transformed to a body-centered tetragonal cell,[15] with $a = 15.2617(28)$ Å and $c = 15.2551(46)$ Å. Data were collected at 291 K in the $\omega-2\theta$ scan mode. Lorentz, polarization, and absorption corrections were applied. Iron, sulfur, and phosphorus positions were initially found by the heavy-atom method in the space group *P*1, which allowed the tetragonal axis to be distinguished in the nearly cubic unit cell. Remaining non-hydrogen atoms were found in successive cycles of full-matrix least-squares refinements on *F* and Fourier difference syntheses. The structure converged with $R = 0.050$, $R_w = 0.057$, and GOF = 1.422 for 1483 reflections. The weighting scheme was $w = 1/[\sigma^2(F_o) + (0.02F_o)^2]$.

Results and Discussion

Crystal Structures of 1−5. The cations in **1** are crystallographically well defined. **2**, presumably **3**, and **4** show some rotational disorder in the butyl groups of the thiolate ligands.[4−6] The inner geometries of the $[Fe_4S_4(S^tBu)_4]^{2-}$ anion cores are very similar[4,6] (see Table 1). In the structures of compounds **1**−**4**, the interactions of the anions with the cations are very similar, with four cations around the $[Fe_4S_4(SR)_4]^{2-}$ anion.[4,6] The structure of compound **5** is unknown but is included in this study because it contains the same anion as compounds **1**−**4** and the same cation as **6**.

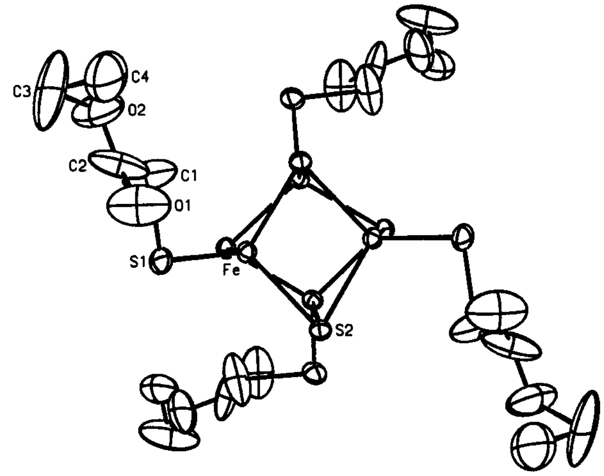

Figure 1. Structure of the $[Fe_4S_4(SCH_2CO_2C_2H_5)_4]^{2-}$ anion showing the atom-labeling scheme with 50% probability ellipsoids.

Table 2. Selected Bond Distances (Å)

Fe−Fe*	2.746(3)	Fe−S(2***)	2.282(3)
Fe−Fe**	2.762(2)	S(l)−C(1)	1.88(2)
Fe−S(l)	2.259(3)	P(l)−C(11)	1.79(1)
Fe−S(2)	2.296(3)	P(2)−C(21)	1.78(1)
Fe−S(2*)	2.278(3)		

[a] Symmetry codes: (*) −*x*, −*y*, *z*; (**) *y*, −*x*, −*z*; (***) −*y*, *x*, −*z*.

Table 3. Selected Bond Angles (deg)[a]

Fe*−Fe−Fe**	60.20(3)	Fe−S(2)−Fe*	73.77(8)
Fe**−Fe−Fe***	59.60(6)	Fe−S(2)−Fe**	74.22(9)
Fe*−Fe−S(l)	142.7(1)	Fe−S(2)−Fe***	74.56(9)
Fe*−Fe−S(2)	52.82(8)	Fe***−Fe−S(2*)	52.78(7)
Fe*−Fe−S(2*)	53.41(9)	Fe***−Fe−S(2***)	53.12(8)
Fe*−Fe−S(2***)	101.01(7)	S(l)−Fe−S(2)	116.4(1)
Fe**−Fe−S(l)	147.9(1)	S(l)−Fe−S(2*)	111.5(1)
Fe**−Fe−S(2)	52.65(7)	S(l)−Fe−S(2***)	116.2(1)
Fe**−Fe−S(2*)	100.61(8)	S(2)−Fe−S(2*)	104.51(9)
Fe**−Fe−S(2***)	52.66(8)	S(2)−Fe−S(2***)	103.2(1)
Fe***−Fe−S(l)	143.4(1)	S(2*)−Fe−S(2***)	103.74(9)
Fe***−Fe−S(2)	100.16(8)	Fe−S(l)−C(l)	102.2(7)

[a] See Table 2 for symmetry codes.

Crystal Structure of $[PPh_4]_2[Fe_4S_4(SCH_2CO_2C_2H_5)_4]$ (6). The structure of the $[Fe_4S_4(SCH_2CO_2C_2H_5)_4]^{2-}$ anion with the atom-labeling scheme[16] is shown in Figure 1. Selected bond lengths and angles are given in Tables 2 and 3. The iron and sulfur, S(2), atoms form the expected $[4Fe\text{-}4S]^{2+}$ cubane-like cluster, centered on the Wyckoff (a) site of $\bar{4}$ symmetry in the space group $I\bar{4}$ (No. 82). The tetrahedron forming this inner core is among the most nearly regular so far found.[17] The

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tetrahedron of the iron atoms is very slightly elongated along the *c* axis, contrasting with a slight flattening of the associated S(2) tetrahedron.[18] The central $[4Fe\text{-}4S]^{2+}$ core has almost perfect $\bar{4}2m$ (D_{2d}) point symmetry, deviating only by a small twist of 0.48° away from perfect staggering between the iron and sulfur tetrahedra. This twist is manifested by the difference between the Fe−S(2) and Fe−S(2*) distances shown in Table 2.

The main structural features of the $[4Fe\text{-}4S]^{2+}$ core are similar to those of the characterized $[Fe_4S_4(S^tBu)_4]^{2-}$ salts and to those of a number of other clusters presented for comparison in Table 1. There are three sets of four equivalent Fe−S(2) bond lengths. The first set, parallel to the $\bar{4}$ direction, is 2.282(3) Å, and there are two sets of bond lengths with an average of 2.287(4) Å lying perpendicular to the $\bar{4}$ axis. The overall mean Fe−S bond length is 2.285(2) Å. This value lies within the range observed[19] in another study (2.278(5)−2.292(10) Å).

All $[4Fe\text{-}4S]^{2+}$ cores show a degree of distortion in the 4-fold axis direction. This distortion has been examined at length, but its origin is still open to discussion. The first attempts to determine the electronic configuration used a perfect cubane core and resulted in orbitally degenerate ground states.[20−22] These conclusions led to the interpretation that the core distortions are a result of a Jahn−Teller effect,[23] but it has also been argued that Jahn−Teller distortion would not lead to a diamagnetic ground state.[24] Theoretical calculations were also applied to this problem using T_d and D_{2d} symmetry restraints,[25] and more recent theoretical calculations used double-exchange and vibronic coupling mechanisms to investigate the electronic states above the diamagnetic ground state.[26]

The atoms of the C_4O_2 chain attached to S(1) manifest large and highly anisotropic thermal ellipsoids. These are ascribed both to large thermal vibration amplitudes and to conformational disorder, as these atoms have a large amount of free space in which to arrange themselves.

The phosphorus atoms lie on Wyckoff sites (b) and (d) of the $I\bar{4}$ space group, and therefore the $[PPh_4]^+$ cations have the maximum point symmetry possible for such species, i.e., $\bar{4}$.

The packing of ions is such that each cluster anion has an irregular array of 10 relatively close cation neighbors, two lying on the *c* axis at distances of 7.628 Å, the four next closest being arranged as a flattened tetrahedron at 8.531 Å, and the remaining four lying in a square further out at 10.792 Å. The resulting coordination number for each anion is thus larger than that for salts **1**−**4**, and the geometrical arrangement of the lattice field is more complex. There are many cation−anion interactions but no close contacts between the anions.

Structural studies of other compounds indicate that solid-state environmental effects play a role in the distortion of the $[Fe_4S_4(S^tBu)_4]^{2-}$ anion core,[4,6] and it was thought that various distortions seen in **1**−**4** could be ascribed not to the ligand environments but to lattice effects.[4] It seems likely that complexities in the anion−cation contacts should be a major contributor to the lattice effects in compound **6**, and it is feasible that the unusually small distortion of the core in **6** could be a consequence of the lattice effects counteracting the usual tendency for the cluster to distort.

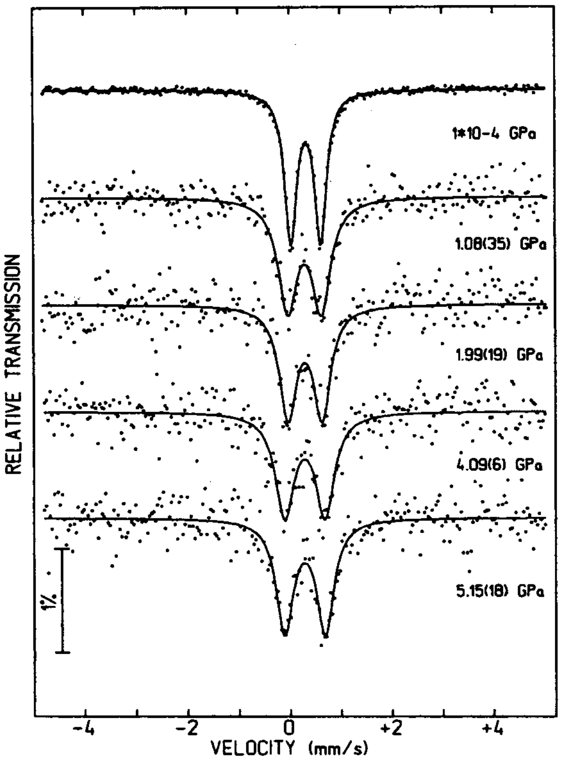

Figure 2. Mössbauer spectra of $[NMe_4]_2[Fe_4S_4(S^tBu)_4]$ (**1**) at 293 K at the pressures indicated.

Mössbauer Spectroscopy. *f* Factors. It can be seen from the high-pressure spectra in Figure 2 and the collection times in Table 4 that the Mössbauer *f* factors (the fraction of ^{57}Fe atoms able to absorb γ-rays and undergo the Mössbauer effect) increase with applied pressure, so that the statistics on the higher pressure spectra are best. *f* factors can in theory be subdivided into many component products, but here it is chosen to discuss the *f* factor as a whole since there is only one experimental *f* factor. The mean vibrational amplitudes of the ^{57}Fe nucleus play the major role in determining the *f* factor. Increased pressure is expected to increase the steepness of the potential well in which the ^{57}Fe nuclei reside. This will decrease the root-mean-square vibrational amplitudes of the ^{57}Fe nuclei in two ways; i.e., the amplitudes of all individual vibrational quantum states are reduced directly, and the energy spacing between states is increased, thereby reducing the thermal population of higher states. Due to the nature of the experiment, the geometry of the gasket hole and sample thickness change when the pressure is changed. This unknown variation of sample geometry prevents full analysis of *f* factor data.

Line Widths ($\Gamma_{1/2}$). Compounds **1**−**3** and **6** all have highly symmetrical anions in which the iron atoms are crystallographically identical. The values for $\Gamma_{1/2}$ at 298 K range from 0.14(1) to 0.22(2) mm/s, the small values confirming single-site spectra. Sample **4** has a larger $\Gamma_{1/2}$ value of 0.32(2) mm/s, which is entirely consistent with the crystal structure,[4] in that the iron sites within the cluster are not symmetry equivalent and four different Fe−S(ligand) distances are quoted. Thus a range of

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Table 4. Mössbauer Spectroscopic Parameters for $[4Fe\text{-}4S]^{2+}$ Salts at Various Temperatures and Pressures

P (GPa)	T (K)	δ^a (mm/s)	ΔE_Q (mm/s)	$\Gamma_{1/2}{}^b$ (mm/s)	collcn time (h)
Compound **1**					
1×10^{-4}	78	0.43(2)	0.72(2)	0.20(2)	
1×10^{-4}	298	0.32(2)	0.59(2)	0.14(1)	19
1.08(35)	293	0.29(2)	0.66(2)	0.22(2)	46
1.99(19)	293	0.29(2)	0.67(2)	0.20(2)	20
4.09(06)	293	0.28(2)	0.79(2)	0.22(3)	19
5.15(18)	293	0.28(2)	0.80(2)	0.20(3)	14
Compound **2**					
1×10^{-4}	78	0.43(2)	1.14(2)	0.23(2)	
1×10^{-4}	298	0.37(2)	0.81(2)	0.22(2)	
$[Me_3NCH_2Ph]_2[Fe_4S_4(S^tBu)_4]$					
	78	0.43	1.10	0.19	
Compound **3**					
1×10^{-4}	78	0.44(2)	1.35(2)	0.16(2)	
1×10^{-4}	298	0.34(2)	0.82(2)	0.22(2)	
0.94(20)	293	0.31(1)	0.83(2)	0.21(2)	36
2.24(13)	293	0.30(1)	0.90(1)	0.22(2)	15
2.95(29)	293	0.36(1)	0.96(1)	0.24(2)	9
4.16(29)	293	0.33(1)	0.96(2)	0.21(3)	16
Compound **4**					
1×10^{-4}	78	0.44(2)	1.36(2)	0.19(2)	
1×10^{-4}	298	0.30(2)	0.91(6)	0.32(4)	124
0.86(2)	293	0.27(2)	0.90(3)	0.21(2)	338
1.99(19)	293	0.29(2)	0.95(2)	0.21(2)	43
4.33(53)	293	0.30(2)	0.95(3)	0.22(5)	12
6.28(03)	293	0.28(1)	0.95(2)	0.23(2)	48
Compound **5**					
1×10^{-4}	78	0.44(2)	0.97(2)	0.17(2)	
1×10^{-4}	298	0.36(2)	0.68(2)	0.18(2)	
1.16(09)	293	0.37(2)	0.80(3)	0.30(4)	22
2.7(39)	293	0.32(1)	0.84(2)	0.29(4)	18
4.45(04)	293	0.36(3)	0.88(3)	0.28(3)	16
Compound **6**					
1×10^{-4}	78	0.43(2)	0.81(2)	0.15(2)	
1×10^{-4}	293	0.36(1)	0.68(2)	0.19(1)	
1.01(28)	293	0.33(1)	0.85(2)	0.20(3)	24
2.43(24)	293	0.27(1)	0.79(3)	0.19(4)	22
3.13(15)	293	0.29(1)	0.85(3)	0.20(3)	19
4.67(15)	293	0.27(1)	0.79(2)	0.21(3)	22
4.68(86)	293	0.28(1)	0.83(2)	0.23(3)	22
4.69(99)	293	0.31(2)	0.79(3)	0.23(4)	23
5.83(30)	293	0.29(2)	0.85(3)	0.26(4)	17

[a] δ = isomer shift, referenced to iron foil at 293 K for high-pressure measurements and at 298 K for others. [b] $\Gamma_{1/2}$ = half-width at half-height.

isomer shifts and ΔE_Q values might be anticipated, although the fact that widely separate sites are not seen in the Mössbauer spectrum shows that localization of valence electrons (giving separate Fe(II) and Fe(III) sites) does not occur.

At elevated pressures (and, at 78 K, atmospheric pressure) the line widths for **1**, **3**, and **4** are roughly constant when due allowance is made for the different sources (room-pressure spectra at both temperatures were recorded with lower activity sources which have narrower natural line widths). In particular, compound **4** shows much sharper lines than it does under ambient conditions, suggesting that the iron sites have in some way become equivalent. More pronounced temperature effects have been discussed elsewhere for $[Fe_6S_6Cl_6]^{2-}$ clusters,[27-30] where a broad room-temperature spectrum was shown to be due to multisite occupancy and at low temperatures the spectrum split into separate sites. This however does not describe the behavior of **4**, since the $\Gamma_{1/2}$ value decreases significantly at low temperature and does not show any sign of resolving into separate sites.

Isomer Shifts (δ). For salts **1** and **6**, the δ values decreased slightly with increasing pressure, suggesting an increase in electron density at the iron nucleus. Similar pressure effects on δ have been seen for other iron compounds.[31] As pressure is expected to reduce volume and thereby cause a general overall increase in electron density, it would be surprising if δ did not decrease with pressure. The δ values for compounds **3**−**5** show little variation with pressure, implying that, in these cases, there is no change in the electron density at the nucleus and that the generally expected increase of electron density is not transmitted to the iron nuclei. It is possible that changes in δ values may be masked by changes in the second-order Doppler effect with pressure. However, pressure-induced changes in second-order Doppler shifts are expected to be small for lattices of low Debye temperature, and a possible relativistic contribution may also be neglected.[32,33] The effects of temperature changes on δ are more apparent in all compounds and consistent with previous data.[34]

Quadrupole Splittings (ΔE_Q). There are contributions to q_{latt} from the cations and from the local sulfur ligands. Bearing in mind the relative distances of the cations and the ligands from the Fe nucleus together with the r^{-3} dependence of the electric field gradient, it seems that the contributions from the cations should be neglected unless it can be shown that the net contribution from ligands is very small. q_{val} in distorted tetrahedral Fe(II) complexes has been shown to be large and very temperature sensitive.[35] This is because the odd electron lies in one of the e orbitals and creates a large field gradient. If the splitting between the e orbitals (d_{z^2} and $d_{x^2-y^2}$) is small and the excited orbital is thermally accessible and is given a favorable molecular vibration, the system can equilibrate between the two states. As they have electric field gradients of opposite signs, the observed ΔE_Q is very temperature sensitive. In the case of the $[FeCl_4]^{2-}$, anion the splitting falls from 3.27 mm/s at 4.2 K to 0.72 mm/s at 293 K.[36]

In the $[Fe_4S_4]^{2+}$ clusters, the iron atoms are of the required distorted tetrahedral geometry but are not Fe(II). However, the iron atoms are in most cases equivalent and can be described as Fe(2.5). Although various bonding and exchange theories may affect detailed descriptions of the system,[26] they must all have equivalent arrangements of electron density at each Fe atom and similar electronic field gradients. In conceptual terms, one may think of each Fe atom as possessing an extra half-electron over the d^5 half-filled symmetric shell of Fe(III), this half-electron causing an electronic field gradient about half of that in the $[FeCl_4]^{2-}$ anion.

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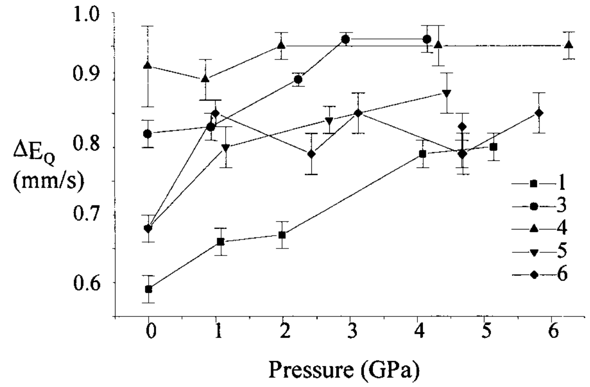

Figure 3. Plot for ΔE_Q at 293 K and at pressures from 1×10^{-4} to 6.28 GPa for compounds **1** and **3**−**6**.

The contribution of ligand atoms to q_{latt} also depends on the tetrahedron being distorted but has a sign opposite that of the corresponding q_{val} for a high-spin d^6 configuration (or $d^{5.5}$) and a smaller magnitude. Variation of ΔE_Q with temperature is described by

$$Q_{\text{obs}} = Q_0(1 - e^{-\Delta/kT})/(1 + e^{-\Delta/kT})$$

where $Q_{\text{obs}} = \Delta E_Q$ of the ground state. Δ is the energy gap between the ground and first excited states. The effect of pressure on this system would be to increase Δ, thereby depopulating the higher state and increasing ΔE_Q.

ΔE_Q is shown to increase with pressure for all compounds (except that of **2**, which was not measured), and the results are plotted in Figure 3. However the pattern of the increase varies considerably. ΔE_Q also increases when the temperature is reduced to 78 K from ambient. Previous Mössbauer spectroscopic studies over the temperature range 78−298 K show similar changes in ΔE_Q.[34,37−41] The $[Fe_6S_6Cl_6]^{2-}$ cluster exhibits structural changes with temperature observable in both the Mössbauer and the crystallographic data;[27] these were attributed to variations in the superexchange and double-exchange coupling constants involving the paramagnetic iron atoms.[28,29]

Both lowering of temperature and raising of pressure are expected to cause lattice contraction. Reduction of the cation−anion distance alone would give rise to an increase of the negative q_{latt}, and hence a reduction in ΔE_Q would be observed. As this is contrary to the observations, it means that any contribution to q_{latt} by the cations is small in relation to larger positive contributions from sulfur ligands. A general effect of increasing pressure and of reducing temperature is to reduce vibrational amplitudes. In particular, reduction in the amplitudes of sulfur ligands would be expected to reduce the mean ligand symmetry around the iron, accounting for the increase in ΔE_Q. In other words, the electronic environment of the iron atoms becomes less nearly tetrahedral.

On considering the compounds **1** and **3**−**5**, it is reasonable that the pattern of the ΔE_Q increase should be no different; this variation clearly must be associated with the properties of the cations. The $[NMe_4]^+$ cation in **1** is relatively small (smaller than the anion), is effectively spherical, and has no torsional vibrational modes for the non-hydrogen atoms. This cation may be thought of as hard. It is therefore difficult to distort or to compress, and its smallness suggests that the pressure effects on **1** will not be very great. There is a change of only 0.13 mm/s in ΔE_Q over this temperature range. The cations are assumed not to distort the lattice; this suggests that the increase in electronic symmetry at the iron is a local effect as described above. On application of higher pressure at room temperature, lattice vibrations must become restricted. Thus pressure squeezes the lattice, and although it still has energy to vibrate, it is able to accommodate the pressure by returning toward the 78 K structure. This is apparent from the gradual increase in ΔE_Q with pressure. At 5.15(18) GPa, the ΔE_Q value becomes even larger than that at 78 K, indicating that the lattice effect has been squeezed past its 78 K value. The molecular vibrations have thus been restricted more than those at 78 K. Compound **1** is therefore defined as a class A salt.

In compounds **3** and **4**, there is a much greater increase in ΔE_Q on cooling to 78 K, but the increase with pressure is less pronounced. The $[NPr_4]^+$ and $[NPen_4]^+$ cations have bulky alkyl chains that are not arranged symmetrically and disorder in the room-temperature structures.[4] By analogy with previous findings at 78 K, it is assumed that the cation lattice effect is minimal;[5] hence the change in ΔE_Q must be solely due to an increase in local symmetry at the iron. In these cases, the change in the q_{latt} component of ΔE_Q is minimal and the overall change with temperature is thereby larger than that for compound **1**. In compounds **3** and **4**, almost all of the ΔE_Q arises from q_{val}. Upon exertion of a 6.28(3) GPa pressure on **4** at room temperature, ΔE_Q increased by only 0.04 mm/s over the atmospheric pressure value. The pentyl chains do not return to their low-temperature orientation under the influence of pressure because they still have energy to vibrate. In these cases, where the cations are quite large and are covered by flexible carbon chains, the major effect of pressure is to compress these chains with a smaller effect on the cluster anion. This explains why there is a smaller observed ΔE_Q value at high pressure compared to the value at 78 K under atmospheric pressure. As compounds **3** and **4** behave in similar ways with pressure, they are assigned to class B. This class is defined as containing large softer cations that disorder at 298 K and allow their respective anions freedom to vibrate when pressure is applied. Compound **2** shows disorder in the cation and also fits into class B.

The $[PPh_4]^+$ cation in **5** is large but rigid when compared with $[NPr_4]^+$ and $[NPen_4]^+$ cations. Here, as in **1**, the effect of pressure on ΔE_Q is fairly large. Curiously, lowering the temperature has a much greater effect on **5** than on **1**, similar to that seen for **2**−**4**. The value at the highest pressure is closer to its 78 K value compared to those of **3** and **4**. This is probably due the fact that **5** is not able to pin the lattice open and vacant space in the lattice is eliminated under pressure. The $[PPh_4]^+$ cation is often found to be highly ordered and well defined in crystal structures, and although the rings can vibrate (as seen in the structure of compound **6**), the cation is more rigid than the $[NPr_4]^+$ cation. Thus, once unoccupied space is eliminated, little further change is manifest in the ΔE_Q value. We therefore put **5** in class C, which is intermediate between the first two classes and contains cations that are symmetric, less prone to distort than class B, but softer than class A.

The cluster anion in **6** is basically different in shape from the others, as the external ligands are five-atom flexible chains. The effect of pressure comprises a rapid increase in ΔE_Q at

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1.01(28) GPa, followed by no further significant change; however, this ΔE_Q value is greater than the 78 K value. A surprisingly small ΔE_Q at both room temperature and 78 K is observed. This suggests the vibrations of the ligand sulfur are immediately restricted, with additional pressure causing no further change. The crystal structure manifested some disorder at the terminus of the $-SCH_2CO_2C_2H_5$ chain, suggesting an amount of free space in the lattice. It is likely that this space is initially lost on the application of pressure and any other changes caused by pressure do not cause further loss of freedom to the electronic environment around the iron atoms. Further squeezing of the lattice must be taken up in a symmetrical way. The anion to cation distances also cannot change further, as this would affect the q_{latt} contribution and hence ΔE_Q, unless coincidentally q_{val} also changes to offset a change in q_{latt}. The overall change in ΔE_Q for compound **6** is similar to that for **5**, but the anion chains require less pressure to alleviate their disorder. Thus compound **6** fits into class C.

Conclusion

It has been demonstrated that the application of pressure at 293 K to these cluster salts distorts the iron environment similarly to a reduction of temperature. In the ordered lattice case (**1**), it was possible to squeeze the lattice back to its ΔE_Q value at 78 K and indeed past this value, thus achieving the original aim of the work. In the case of the disordered lattices (**3**−**6**), this was not possible. A plausible explanation of how high pressure affects ΔE_Q values for $[4Fe\text{-}4S]^{2+}$ clusters has been put forward whereby q_{latt} for the ligand sulfur atoms is important. Three distinct types of lattice have been identified. Class A has a “hard” lattice and is found in the highly ordered lattice case, in which the cations can be thought of as hard spheres that do not distort with temperature in the range 78−298 K or with pressure up to at least 5.15(18) GPa. Class B contains softer cations that display disorder at 298 K and keep the lattice pinned open when pressure is applied, effectively protecting the cluster cores from the external pressure. Class C is intermediate between the first two and contains cations that are symmetric, less likely to distort than class B, but softer than class A.

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Supporting Information Available: The matrix transformation used for conversion of the data from $P1$ to $I\bar{4}$ and an X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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