Synthesis and Proton Magnetic Resonance Properties of Fe₃MS₄ (M = Mo or W) Cubane-like Cluster Dimers

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Synthetic procedures leading to the preparation of the complexes [Fe₃M₂S₈(SR)₉]³⁻ (where M = Mo and R = Ph, C₆H₅Cl·p, C₆H₅Me·p, or Et; or M = W and R = Et) and [Fe₃M₂S₈(OMe)₉]³⁻ (where M = Mo or W) are detailed. 300 MHz ¹H n.m.r. spectra have been recorded for these complexes and [Fe₃Mo₃S₈Cl₄(SR)₉]³⁻ (where R' = Et or Ph) in [²H₆]dimethyl sulphoxide at temperatures between ca. 20 and 80 °C. For all complexes, a clear distinction between bridging and terminal ligands is observed and, within each set of bridging and terminal ligands, only one resonance is observed for each chemically different proton. The bridging ligands exhibit much smaller isotropic shifts than those for the corresponding ligands in the terminal positions and all of the shifts decrease in magnitude with an increase in temperature. The isotropic shifts of the terminal ligands appear to be predominantly contact in origin via a π- (arylthiolato-groups) or σ- (alkylthiolato-groups) spin delocalisation mechanism; however, for the bridging region both contact and dipolar mechanisms seem to be operative, the latter being of particular importance for the μ₂-methoxo-bridged complexes.

In recent communications we have reported the synthesis,³⁻⁵ structural characterisation,¹⁻⁵ and some preliminary physicochemical,⁶⁻⁷ and chemical properties of a range of complexes of general formulation [NR₄]₃⁻ [Fe₉S₈(SR')₉] (R = Et or Bu⁺; R' = Et, Ph, or CH₂CH₂OH; M = Mo or W), type I, and [NEt₄]₃⁻ [Fe₉S₈(SPh)₆(OOMe)₃] (M = Mo or W), type II. These contain two Fe₉S₈ cubane-like clusters bridged between their M atoms by three μ₄-thiolato-groups (Figure 1) or three μ₂-methoxo-groups. These systems may be considered as structural derivatives of the well characterised [Fe₄S₄]⁴⁻ clusters,⁶⁻⁷ inasmuch as the substitution of one iron atom by a molybdenum atom causes little change in the dimensions of the cubane-like core.¹⁻⁵ An important aspect of the Fe₉MoS₈ cluster systems is that they contain molybdenum in an environment very similar to that suggested for this atom in nitrogenase and its iron–molybdenum cofactor.¹⁰ Although subsequent¹¹ elemental analyses for this cofactor indicate a Mo:Fe:S ratio of 1:6–8:4–6, e.x.a.f.s. (extended X-ray absorption fine structure) studies⁸⁻⁹ have suggested that the molybdenum is adjacent to three or four sulphur atoms, at a distance of 2.35 ± 0.03 Å, and two or three iron atoms, at a distance of 2.72 ± 0.05 Å, features which bear a striking resemblance to the Mo–S and Mo–Fe contacts within the Fe₉MoS₈ clusters (I and II).¹⁻⁵ Although other structural interpretations have also been placed on the e.x.a.f.s. data,⁹⁻¹² we consider the occurrence of an Fe₉MoS₈ system an attractive possibility and have initiated an extensive programme of physicochemical studies on complexes of types I and II. Herein, we report the synthesis and proton n.m.r. studies, which were undertaken principally to investigate the influence of the electronic properties of the Fe₉MS₄ core(s) on the n.m.r. spectra of the ligands. In addition, we have sought to characterise the differing n.m.r. behaviour of bridging and terminal ligands and have compared the data obtained with those of the [Fe₉S₄(SR)₉]⁴⁻⁻⁻⁻ complexes.¹³⁻¹⁴

EXPERIMENTAL

All reactions and manipulations were performed in standard Schlenk-type apparatus under an atmosphere of purified dinitrogen passed over a column of deoxygenation catalyst BASF R3-11 at 140–150 °C. Solution transfers were made by nitrogen-flushed glass syringes and steel needles through rubber spectrum caps (Gallenkamp). All solvents were degassed prior to use by repeated vacuum–nitrogen cycles: AnalR methanol and ethanol were used as obtained, reagent-grade acetonitrile was distilled from CaH₂, tetrahydrofuran was distilled from CaH₂–CuCl₂. Anhydrous iron(III) chloride, tetra-alkylammonium halides, and thiols were used as obtained.

Unless otherwise stated, ¹H n.m.r. spectra were run at 300 MHz on a Varian SC-300 spectrometer. Samples were prepared in [²H₆]dimethyl sulphoxide (dmos) containing hexamethyldisiloxane (hmd) as an internal reference. Chemical shifts are quoted relative to SiMe₄ (δ hmd = 0.00) using the delta scale, in which shifts downfield are positive, in contrast to the opposite sign convention of related work.¹⁵⁻¹⁶ Isotopic shifts were calculated from relationship (1), where (ΔH/ΔH)dia is the corresponding chemical shift of the free ligand:¹⁵⁻¹⁶

\[ (\Delta H/\Delta H)_{dia} = (\Delta H/\Delta H)_{free} - (\Delta H/\Delta H)_{dia} \] (1)

[NBu₄]₃⁻[Fe₉Mo₃S₈(SPh)₉] (1).—Sodium (0.92 g, 40 mmol) was dissolved in MeOH (40 cm³) and the solution cooled to room temperature. Benzenethiol (4.11 cm³, 40 mmol) was added, followed by a solution of iron(III) chloride (1.62 g, 10 mmol) in MeOH (20 cm³). After stirring for a few moments, a deep yellow-black solution was obtained. Addition of solid ammonium thiomolybdate (0.87 g, 3.3 mmol) resulted in the rapid formation of a deep red-brown solution which was stirred overnight at room temperature and filtered into a solution of [NBu₄]I (3.69 g, 10 mmol) in MeOH (20 cm³) to give an immediate black precipitate. This was collected by filtration, washed with MeOH, and dried in vacuo. The crude solid was dissolved in MeCN (ca. 50 °C), filtered, and MeOH added at this temperature to incipient crystallisation. Slow cooling to −5 °C gave the product as large diamond-shaped crystals in 60–70% yield (Found: C, 49.1; H, 6.2; Fe, 13.2; Mo,
7.6; N, 1.7; S, 21.7. Calc. for C₃H₁₅Fe₂Mo₁₅N₅S₁₇: C, 49.1; H, 6.2; Fe, 13.4; Mo, 7.7; N, 1.7; S, 21.9%. 

[NEt₄]⁺[Fe₅Mo₃S₁₀(SC₄H₄Cl⁻)]⁻ (2).—This compound was prepared in a manner completely analogous to that detailed for (1), using p-chlorobenzensulphide (5.78 g, 40 mmol). The material was obtained as small red-black crystals in 63% yield after crystallisation from MeCN-MeOH (Found: C, 43.5; H, 5.15; Cl, 11.5; Fe, 12.1; Mo, 7.2; N, 1.6; S, 19.2. Calc. for C₃H₁₇Fe₅Mo₃S₁₀N₁: C, 43.7; H, 5.2; Cl, 11.4; Fe, 12.0; Mo, 6.8; N, 1.5; S, 19.4%).

[NEt₄]⁺[Fe₅Mo₃S₁₀(SC₄H₄Me⁻)]⁻ (3).—This compound was prepared in a manner similar to that described for (1), using toluene-4-thiol (4.97 g, 40 mmol) and [NEt₄]Br (2.10 g, 10 mmol), and obtained as large black needles in 49.1% yield following crystallisation from MeCN-MeOH (Found: C, 45.8; H, 5.4; Fe, 14.9; Mo, 8.1; N, 1.8; S, 23.9. Calc. for C₃H₁₇Fe₅Mo₃N₅S₁₀: C, 45.8; H, 5.4; Fe, 14.7; Mo, 8.4; N, 1.8; S, 23.9%).

[NEt₄]⁺[FeW₂S₄(SPh)₆(OMe)₃]⁻ (4).—The anion of this complex was obtained in a manner similar to that described for (1), except that ammonium thiotungstate was used. A deep red solution was obtained initially which slowly became orange-brown on standing overnight at room temperature. Filtration into [NEt₄]Br (2.10 g, 10 mmol) gave an oily black precipitate which solidified on standing with occasional agitation. The fine solid was filtered off, washed copiously with MeOH, and dried in vacuo. Crystallisation from warm (ca. 50 °C) MeCN-MeOH gave black needles in 40% yield (Found: C, 35.9; H, 4.7; Fe, 15.9; N, 2.0; W, 17.4. Calc. for C₃H₃₀Fe₅Mo₄N₅O₅W₂S₄: C, 36.1; H, 4.8; Fe, 16.0; N, 2.0; W, 17.5%).

[NEt₄]⁺[Fe₅Mo₃S₁₀(SPh)₆(OMe)₃]⁻ (5).—A solution of sodium (0.78 g, 34 mmol) in MeOH (40 cm³) was treated using toluene-4-thiol (24 cm³, 24 mmol), followed by a solution of iron(II) chloride (1.62 g, 10 mmol) in MeOH (29 cm³) to give a dark brown solution. Addition of solid ammonium thiomolybdate (0.87 g, 3.3 mmol) caused the rapid formation of an intense orange-brown solution which was stirred overnight at room temperature. Filtration into [NEt₄]Br (2.10 g, 10 mmol) in MeOH (20 cm³) gave a sticky black solid which was filtered off, washed copiously with MeOH, and dried in vacuo. Crystallisation from MeCN-MeOH (ca. 50 °C) as black needles in 33% yield (Found: C, 35.9; H, 4.7; Fe, 15.9; N, 2.0; W, 17.4. Calc. for C₃H₃₀Fe₅Mo₄N₅O₅W₂S₄: C, 36.1; H, 4.8; Fe, 16.0; N, 2.0; W, 17.5%).

[NEt₄]⁺[Fe₅Mo₃S₁₀(SPh)₆(OMe)₃]⁻ (6).—A solution of Na[SET] in MeOH (60 cm³) was prepared from sodium (1.84 g, 80 mmol) and ethanethiol (7.15 cm³, 80 mmol). Addition of iron(III) chloride (3.24 g, 20 mmol) in MeOH (20 cm³) gave an immediate green precipitate which slowly dissolved on addition of solid ammonium thiomolybdate (1.74 g, 6.67 mmol) to give a golden brown solution. This was stirred overnight at room temperature and filtered into a solution of [NEt₄]Br (3.15 g, 15 mmol) in MeOH (20 cm³) to give rapid crystallisation of long black needles. After ca. 1 h at 5 °C, the product was collected by filtration, washed copiously with EtOH and Et₂O, and dried in vacuo. The crude material can be recrystallised from MeOH or MeCN-tetrahydrofuran as long needles in 40—60% yield (Found: C, 29.5; H, 6.2; Fe, 19.2; Mo, 11.0; N, 2.2; S, 31.4. Calc. for C₃H₁₅Fe₅Mo₃N₅S₁₀: C, 29.3; H, 6.1; Fe, 19.4; Mo, 11.1; N, 2.4; S, 31.6%).

[NEt₄]⁺[Fe₆W₂S₆(SEt)₆]⁻ (7).—This complex was prepared and recrystallised in a similar manner to its molybdenum analogue, using ammonium thiotungstate (2.32 g, 6.67 mmol), except that the [NET₄]Br was dissolved in EtOH (30 cm³) and the solution kept at —5 °C overnight to ensure maximum crystallisation of the crude product. Yield 30—50% (Found: C, 26.5; H, 5.6; Fe, 17.4; N, 2.1; S, 28.9; W, 19.0. Calc. for C₃H₁₅Fe₆W₂S₆: C, 26.6; H, 5.6; Fe, 17.6; N, 2.2; S, 38.7; W, 19.4%).

RESULTS AND DISCUSSION

Synthesis of Complexes.—The synthetic route to the type I compounds, (1)—(3), (6), and (7), is summarised in Scheme 1. Although other ratios of iron(III): thioldioxide: molybdenum were used (M = Mo), including 1:10 for PhSH, the predominant reaction products did not change. The type II complex [NEt₄]⁺[Fe₆W₂S₆(SPh)₆(OMe)₃] (4) was prepared in a manner completely analogous to that for (1); this incorporation of methoxo-groups into the bridging positions in preference to thioliato-groups is remarkable, given (i) the successful syntheses of (1) and (7), (ii) the initial absence of MeO⁻, and (iii) the presence of an excess of PhS⁻. Recrystallisation of the crude material (4) from MeCN instead of MeCN-MeOH also gave an analytically pure sample, thus indicating that the methoxo-groups are incorporated in the reaction mixture, rather than during recrystallisation. To our knowledge, the only other characterised complex containing the W(OMe)₃W bridging unit is [(η⁵-C₅H₅)(CO)₃W(OMe)₃W(CO)(η⁴-C₄H₄)]₁₈. In contrast to the ready incorporation of η₂-methoxo-groups in (4), the substitution of η₂-benzenethiolato-groups of (1) by methoxide ions proved difficult and a direct synthetic procedure was therefore developed to prepare (5). The initial iron : benzenethiol ratio was reduced to a level (6 : 14) such that only sufficient of the latter was present for terminal ligation and reduction of the metal atoms; in addition, an excess of methoxide ions was present in the reaction mixture (Scheme 2). An X-ray crystallographic study of the product has confirmed the success of this scheme.
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synthetic approach; [NET₄]₃[Fe₆Mo³S₆(SPh)₆(OMe)₃] is isomorphous with its tungsten analogue with an Mo···Mo separation of 3.142(3) Å.

**Hydrogen-1 N.M.R. Spectra.**—Studies have been accomplished for the compounds (1)–(7) in [²H₆]dmso at ca. 23, 50, and 80 °C. These complexes include variations in a metal atom (Mo vs. W), the terminal and bridging thiolato-groups, and the μ₂-bridging ligands (thiolato- or methoxo-). Some n.m.r. spectral data have also been included for the hitherto unreported compounds [NR₄]₃[Fe₆Mo₂S₆Cl₆(SR')₃] (R = R' = Et or R = Me, R' = Ph) and have provided confirmation of the spectral assignments suggested for the above compounds.

The ¹H resonances for the cations were as expected and showed almost no temperature dependence or paramagnetic broadening or shifting. The anions of complexes (1) to (7) exhibited only one set of resonances for the bridging (B) and one set of resonances for the terminal (T) ligands and, within each set, only one resonance was observed for each type of proton. This suggests that, in solution, all the bridging ligands are equivalent but are chemically distinct from all the terminal ligands, with no rapid exchange occurring between the two types of group. Such a conclusion is in accord with the results of X-ray crystallographic studies which established that the anions of [NET₄]₃[Fe₆Mo₂S₆(SEt)₃]³⁻ and [NET₄]₃-[Fe₆Mo₂S₆(SPh)₆(OMe)₃]⁵⁻ (M = Mo or W) have C₃₅

![](image)

**Figure 1** Framework of the [Fe₆Mo₃S₆L₆]³⁻ (M = Mo or W) cubane-like cluster dimers

![](image)

**Figure 2** 300 MHz ¹H n.m.r. spectra of [Fe₆Mo₃S₆(SPh)₆]³⁻ in [²H₆]dmso (solvent peaks marked by ×)


by methoxy-groups; (iii) the (probable) replacement of terminal benzenethiolato-groups by chloride; and (iv) the relative line widths of the peaks assuming $o > m > p$, corresponding to their relative proximities to the paramagnetic centre(s). The resonance corresponding to the ortho protons of the terminal ligands $(o_T)$ of $\left[\text{Fe}_6\text{Mo}_2\text{S}_6(\text{SPh})_9\right]^{3-}$ was not well resolved (Figure 2); however, it was observed in the corresponding para-substituted complexes, as illustrated in Figure 4 where the para-methyl resonance is also apparent. For the ethanethiolato-complexes, the bridging and terminal ligand resonance positions follow from a comparison of the spectra of $\left[\text{Fe}_6\text{Mo}_2\text{S}_6(\text{SEt})_9\right]^{3-}$ and $\left[\text{Fe}_6\text{Mo}_2\text{S}_6\text{Cl}_9(\text{SEt})_9\right]^{3-}$, on the assumption that the latter probably contains only $\mu_2$-thiolato-groups. The resonances assigned to terminal ligands in the spectrum of the former are absent in the spectrum of the latter. The methyl vs. methylene proton assignment was accomplished by analogy with that $^{13}$ of $\left[\text{Fe}_4\text{S}_4(\text{SEt})_4\right]^{2-}$, i.e. the shift from the diamagnetic position was taken to be greater for the methylene than for the methyl protons.

The isotropic proton shifts for the anions are summarised in Tables 1, 3, and 4 and representative spectra are reproduced in Figures 2, 4, 5, 7, and 8. The isotropic shifts of $\left[\text{Fe}_6\text{Mo}_2\text{S}_6(\text{SPh})_9\right]^{3-}$ are compared with those $^{13,14}$ of $\left[\text{Fe}_4\text{S}_4(\text{SPh})_4\right]^{2-}$ in Table 2. The temperature dependences of the resonance positions of $\left[\text{Fe}_6\text{Mo}_2\text{S}_6(\text{SC}_{6}\text{H}_4\text{R}-\text{p})_9\right]^{3-}$ (R = H, Me, or Cl), $\left[\text{Fe}_6\text{Mo}_2\text{S}_6(\text{SPh})_9(\text{OMe})_9\right]^{3-}$ ($\text{M} = \text{Mo}$ or W), and $\left[\text{Fe}_6\text{Mo}_2\text{S}_6(\text{SEt})_9\right]^{3-}$ (M = Mo or W) are indicated in Figures 3, 6, and 9, respectively; Figure 10 illustrates a comparison between the temperature dependence of the solid-state magnetic susceptibility $^{17}$ of $\left[\text{NBu}_4\right]_2\left[\text{Fe}_6\text{Mo}_2\text{S}_6(\text{SPh})_9\right]$ and the $\delta_T$ and $\rho_T$ isotropic shifts of this anion.

The total isotropic shift of a proton resonance from its diamagnetic position may be expressed as (2),

\[
\frac{\Delta H}{H_0} \text{iso.} = \frac{\Delta H}{H_0} \text{con.} + \frac{\Delta H}{H_0} \text{dip.} \tag{2}
\]

by methano-groups; (iii) the (probable) replacement of terminal benzenethiolato-groups by chloride; and (iv)

\[
\begin{align*}
\delta_T & = 12.57 \\
\rho_T & = 11.33 \\
\gamma_T & = 8.05 \\
\mu_T & = 5.91 \\
\psi_T & = 3.80 \\
\phi_T & = 1.78
\end{align*}
\]
Temperature dependences of the isotropic $^1$H n.m.r. shifts of $[\text{Fe},\text{Mo},\text{S},(\text{SC},\text{H},\text{K-p})_{\text{coiiim}}]$ complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\theta$, $^\circ$C</th>
<th>$\delta_T$</th>
<th>$m_T$</th>
<th>$p_T$</th>
<th>$\delta_B$</th>
<th>$m_B$</th>
<th>$p_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R = \text{H}$</td>
<td>23</td>
<td>$c$</td>
<td>-11.44</td>
<td>1.05</td>
<td>-1.84</td>
<td>1.41</td>
<td>1.84</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>$c$</td>
<td>-10.42</td>
<td>0.89</td>
<td>-1.30</td>
<td>1.62</td>
<td>1.62</td>
</tr>
<tr>
<td>$R = \text{Cl}$</td>
<td>81</td>
<td>$ca.$</td>
<td>-9.0</td>
<td>0.75</td>
<td>-1.24</td>
<td>1.46</td>
<td>1.46</td>
</tr>
<tr>
<td>$R = \text{Me}$</td>
<td>23</td>
<td>$c$</td>
<td>-10.83</td>
<td>6.58</td>
<td>0.30</td>
<td>-1.19</td>
<td>1.19</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>$c$</td>
<td>-9.23</td>
<td>6.00</td>
<td>0.26</td>
<td>-1.19</td>
<td>1.19</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>$c$</td>
<td>-9.03</td>
<td>5.54</td>
<td>0.24</td>
<td>-1.16</td>
<td>1.16</td>
</tr>
<tr>
<td>$R = \text{NMe}_2$</td>
<td>23</td>
<td>-10.78</td>
<td>6.61</td>
<td>11.01</td>
<td>1.26</td>
<td>-1.39</td>
<td>2.12</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>-9.89</td>
<td>6.00</td>
<td>9.99</td>
<td>1.00</td>
<td>-1.29</td>
<td>1.82</td>
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<tr>
<td></td>
<td>81</td>
<td>-8.89</td>
<td>5.46</td>
<td>9.09</td>
<td>0.94</td>
<td>-1.20</td>
<td>1.56</td>
</tr>
</tbody>
</table>

* In $[\text{H}_2]\text{dmso}$; $\pm 0.02$ p.p.m.  
$\dagger$ $[\text{NBu}_4]^+$ salt.  
* Obscured.  
$^a$ Poorly resolved.  
$\dagger$ para-Methyl group.  
$\ddagger$ $[\text{NEt}_4]^+$ salt.

**Table 2**
Comparison of the isotropic shifts of $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{3-}$ with $[\text{Fe}_4\text{Mo}_2\text{S}_4(\text{SPh})_2]^{3-}$ terminal-ligand shifts

<table>
<thead>
<tr>
<th>Complex</th>
<th>Isotropic shift $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Fe}_4\text{Mo}_2\text{S}_4(\text{SPh})_2]^{3-}$</td>
<td>$\delta$ = 6.61, $m$ = -11.44, $p$ = 1.05</td>
</tr>
<tr>
<td>$[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{3-}$</td>
<td>$\delta$ = 3.30, $m$ = -5.55, $p$ = 1.25</td>
</tr>
<tr>
<td>$[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{3-}$</td>
<td>$\delta$ = -1.56, $m$ = 0.89, $p$ = -2.09</td>
</tr>
</tbody>
</table>

* Temperature 22–23 $^\circ$C; $\pm 0.02$ p.p.m.  
$^a$ $[\text{H}_2]\text{dmso}$; $[\text{NBu}_4]^+$ salt.  
$^b$ $[\text{NBu}_4]^+$ salt; ref. 14.  
$^c$ Not observed but $ca.$ $-8.4$ in $[\text{H}_2]\text{MeCN}$; $[\text{NBu}_4]^+$ salt; ref. 15.  
$^d$ Poorly defined; $[\text{NEt}_4]^+$ salts.

**Table 3**
Comparison of the isotropic shifts of $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{3-}$ with the solid-state magnetic susceptibility ($\chi$) of $[\text{NBu}_4]^+[\text{Fe}_4\text{Mo}_2\text{S}_4(\text{SPh})_2]$ (Table 5, Figure 10). Therefore, we conclude that the isotropic shifts of the terminal-ligand aromatic protons in these cubane-like cluster dimers is predominantly, if not exclusively, contact in origin. The pattern of the contact shifts is similar to that observed for other complexes with contact-shifted aromatic protons and is suggestive of ligand-to-metal antiparallel spin transfer resulting in parallel spin alignment in the sulphur lone-pair orbitals which is delocalised around the $\pi$ system of the aromatic ring in the manner described for $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{3-}$ and $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{3-}$.

**Figure 5**
300 MHz $^1$H n.m.r. spectrum of $[\text{Fe}_4\text{W}_2\text{S}_4(\text{SPh})_4(\text{OMe})_4]^{3-}$ in $[\text{H}_2]\text{dmso}$ at ca. 23 $^\circ$C (solvent peaks marked by $\times$)
of [Fe₆Mo₂S₈(SEt)₆]³⁻ and the other arylthiolato-complexes are greater than those of [Fe₄S₄(SEt)₄]²⁻ complexes, the ratio of shift values (CH₃:CH = 1:0.064) for the former is similar to that (1:0.110) for the latter; the shifts of the latter are also considered to be predominantly contact in origin. Similar attenuation rates have also been observed for nickel(II) complexes of alkyl ligands.¹⁰,¹²

**Bridging ligands.** The n.m.r. shifts of the bridging ligands do not follow the patterns observed for the alkyl or aryl groups of the terminal ligands. This is seen most clearly for [Fe₆Mo₂S₈(SPh)₆(OMe)₃]³⁻ (M = Mo or W) complexes (Table 3, Figure 5), in which the methoxide resonances (ca. −3.3 p.p.m. at 50 °C) are shifted markedly upfield. This is not consistent with a contact shift effect and, in common with other complexes with upfield shifted alkyl-methyl groups,¹⁴ is attributed to a dominant dipolar contribution. In contrast, the bridging ligand isotropic shifts for the [Fe₆Mo₂S₈(SEt)₆]³⁻ complexes (Table 4, Figure 7) [CH₂B, 13.6 (Mo) and 9.0 (W); CH₃ ca. −0.1 at 50 °C] are taken to indicate that both contact and dipolar effects are operative, with the former being the major contributor for the methylene shifts, whereas the net upfield shift of the methyl resonances is presumably due to the dipolar contribution dominating at this position. The reason(s) for the difference in sign between the isotropic shifts for the protons of the −OCH₃ and −SCH₂- bridging groups is (are) unclear. A major factor could be the change in the nature of the bridging atom affecting the relative importance of the σ-contact and dipolar-shift mechanisms; if so, the results obtained here would

**TABLE 4**

Temperature dependences of the isotropic ¹H n.m.r. shifts of [Fe₆Mo₂S₈(SEt)₆]³⁻ (M = Mo or W) complexes

<table>
<thead>
<tr>
<th>Isotropic shift</th>
<th>Complex</th>
<th>0/°C</th>
<th>CH₃ &amp;</th>
<th>CH₂ &amp;</th>
<th>CH₃ T</th>
<th>CH₂ T</th>
<th>CH₃ B</th>
<th>CH₂ B</th>
<th>CH₃ A</th>
<th>CH₂ A</th>
<th>CH₃ B</th>
<th>CH₂ B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[Fe₆Mo₂S₈(SEt)₆]³⁻</td>
<td>23</td>
<td>52.86</td>
<td>14.98</td>
<td>3.37</td>
<td>c</td>
<td>50</td>
<td>48.7</td>
<td>13.6</td>
<td>3.29</td>
<td>−0.13</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>[Fe₆W₂S₈(SEt)₆]³⁻</td>
<td>23</td>
<td>51.35</td>
<td>9.89</td>
<td>3.22</td>
<td>c</td>
<td>50</td>
<td>47.51</td>
<td>8.99</td>
<td>3.14</td>
<td>c</td>
<td>80</td>
</tr>
</tbody>
</table>

* [¹H]dmso; ±0.02 p.p.m. ¹ Assignments tentative.

**TABLE 5**

Temperature dependences of terminal-ligand isotropic shifts and solid-state magnetic susceptibility (χ) of [NB₄][Fe₆Mo₂S₈(SPh)₆]

<table>
<thead>
<tr>
<th>θ/°C</th>
<th>10³ χ/°(cm² mol⁻¹</th>
<th>oT²</th>
<th>mT</th>
<th>pT</th>
<th>χ</th>
</tr>
</thead>
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<tr>
<td>23</td>
<td>13.71</td>
<td>−10.78</td>
<td>6.61</td>
<td>11.44</td>
<td>1.000</td>
</tr>
<tr>
<td>35</td>
<td>13.18</td>
<td>−9.89</td>
<td>5.97</td>
<td>10.42</td>
<td>1.000</td>
</tr>
<tr>
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<td>12.59</td>
<td>−9.89</td>
<td>5.97</td>
<td>10.42</td>
<td>1.000</td>
</tr>
<tr>
<td>60</td>
<td>12.23</td>
<td>−9.89</td>
<td>5.97</td>
<td>10.42</td>
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</tr>
<tr>
<td>80</td>
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<td>−9.89</td>
<td>5.97</td>
<td>10.42</td>
<td>1.000</td>
</tr>
<tr>
<td>90</td>
<td>11.23</td>
<td>−9.89</td>
<td>5.97</td>
<td>10.42</td>
<td>1.000</td>
</tr>
</tbody>
</table>

* Extrapolated from 1.8—297.2 K data. ¹ Relative to value at 323.15 K. ² Quoted values are the unobscured oT of [Fe₆Mo₂S₈(SPh)₆]³⁻. ³ Defined at 90 MHz.
suggest that the former mechanism is the more effective with sulphur, as compared to oxygen, bridging atoms. Another important factor could be the different M···M separations, which are ca. 3.66 Å for three -SR bridging groups and ca. 3.16 Å for three -OMe bridging groups. Although the X-ray crystallographic data \(^{14,16}\) indicate that the shortest H···M approaches for the bridging -OMe and -SCH\(_2\) groups are approximately equal, the electronic structure of the bridging region may be significantly different in the two systems, since a separation of 3.66 Å precludes any direct M-M interaction whereas a separation of 3.16 Å does not. Any such
change in the nature and/or extent of the M⋯M interaction could manifest as a change in the proton isotropic shifts of the bridging ligands.

For the arylthiolato-bridging groups, the respective upfield and downfield shifts of the para and the meta methyl protons (Table 1, Figures 2 and 4) are consistent with a π-contact shift mechanism. This indicates that, for these protons distant from the metal centres, this mechanism is the major contributor to their total isotropic shift. The mechanism responsible for the shift of the ortho and meta protons is, however, less straightforward. If (Table 1) the resonances whose isotropic shifts are ca. 1.2 and in the range 0.2−1.2 p.p.m. are taken to be due to the ortho and meta protons, respectively, the complete sequence of the arylthiolato-n.m.r. shifts would be consistent with a dominant π-contact shift mechanism with the actual shifts being similar to those observed for [Fe₄S₄(SR)₄]²⁻ complexes (Table 2). However, this interpretation neglects the fact that the resonance with isotropic shift in the range 0.2−1.2 p.p.m. is appreciably broader than that with a shift of ca. 1.2 p.p.m. (Figures 2 and 4). Thus, we favour the alternative assignment, with the former feature being attributed to the ortho and the latter feature to the meta proton resonances (Table 1). This pattern of aryl proton resonances is not that expected for a dominant π-contact mechanism and, if this latter assignment is correct, the net downfield shift of the ortho protons could be due to a σ-contact contribution. The upfield shift of the meta protons could be due to a dipolar effect, as postulated for the bridging OMe groups; any σ-contact shift effect would be attenuated at the meta position. Therefore a possible interpretation of the n.m.r. resonances for the bridging arylthiolato-groups requires σ and π contact and dipolar mechanisms to be operative, with the relative importance varying from ortho (σ-contact greatest) to meta (dipolar effect greatest) and para (π-contact greatest) positions. It is observed that, although substitution in the para position only affects the ortho and meta resonances of the terminal ligands to a slight extent, it produces a significant shift in the ortho and, to a certain extent, the meta resonance of the bridging ligand (Table 1). This may be a consequence of a difference in the mechanisms which dominate the various proton isotropic shifts.

For all of the complexes, the magnitude of the n.m.r. isotropic shifts for the terminal ligands from their diamagnetic positions are much greater than those for the bridging ligands. Given that the n.m.r. isotropic shift will be related to the unpaired electron spin density on the paramagnetic centre to which the ligand is bonded (for π- and σ-contact shift mechanisms) or, among other factors, to the proximity of the proton to the unpaired electron spin density (for the dipolar mechanism), the relative magnitudes of the shifts imply that there is less unpaired electron spin density on the molybdenum or tungsten atoms than the iron atoms. A simple qualitative rationalisation of this is afforded by a consideration of the individual metal spin states with reference to the Mössbauer results obtained for these complexes, which indicate a net oxidation state for the iron atoms of ca. 2.5 and, hence, a net oxidation state for the molybdenum (or tungsten) atoms of ca. 3.5. Thus, in the approximately tetrahedral ligand field of the four sulphur atoms, the electronic configuration of the iron atoms will be FeT⁰ (e⁰, t²3) or FeT¹(e², t²) with...
S = 2 or ½, respectively; the molybdenum (or tungsten) atom in the approximately octahedral field of the six sulphur atoms is expected to have an electronic configuration of Mo^{11+} (t_{2g}^3) or Mo^{IV} (t_{2g}^2) with S = ½ or 1, respectively. These spin states will be reduced by spin-pairing effects via direct metal-metal bonding and/or exchange effects transmitted by the bridging ligand atoms, and the actual values will depend upon the extent of these various Fe-Fe, Fe-M, and M-M (M = Mo or W) couplings. Nevertheless, it would appear that the spin pairing interactions do not affect the relative magnitude of the unpaired electron spin density on the iron and the molybdenum (or tungsten) atoms. Furthermore, we note (Tables 3 and 4) that the shifts for all of the ligands in the complexes with tungsten are less than those for the corresponding complexes with molybdenum, consistent with the expected sense of the spin-pairing effects, W-W > Mo-Mo and W-Fe > Mo-Fe.

Conclusions.—The principal results obtained from these n.m.r. studies of the molybdenum (or tungsten) iron–sulphur cubane-like cluster dimers are: (i) for all complexes, a clear distinction of the bridging and terminal ligands is apparent; (ii) within each set of three bridging and each set of six terminal ligands, one resonance is observed for each chemically different proton; (iii) the isotropic shifts for the protons of the bridging ligands are much less than those for the corresponding ligands in the terminal positions; (iv) the isotropic shifts of the protons of the tungsten complexes are slightly smaller than the corresponding ones for the molybdenum complexes; (v) all of the isotropic shifts decrease in magnitude with an increase in temperature; and (vi) the isotropic shifts of the terminal ligands appear to be predominantly contact in origin via a π (for arylthiolato-groups) or σ (for alkylthiolato-groups) spin-delocalisation mechanism; however, for the bridging region both contact and dipolar mechanisms seem to be operative, the latter being of particular importance for the μ2-methoxy-bridged complexes.

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