Binding of the $\{MoFe_3S_4\}^{3+}$ Core by a Tridentate Thiolate and Chemical Analogues of the Molybdenum Co-ordination Environment in the Iron–Molybdenum Cofactor of Nitrogenase

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The tridentate thiol 1,4,7-tris(4-sulfanylbenzoyl)-1,4,7-triazacyclononane (H_3L) on deprotonation ligated to each of the molybdenum–iron–sulfur clusters $[NEt_4][MoFe_3S_4(SEt)_4(dmpe)]$ **1** [dmpe = 1,2-bis(dimethylphosphino)ethane] and $[NEt_4]_2[MoFe_3S_4(SEt)_3(tccat)(solv)]$ [H_2tccat = 3,4,5,6-tetrachlorocatechol; solv = dimethyl sulfoxide (dmso) or MeCN], with elimination of ethanethiol, to give $[NEt_4][MoFe_3S_4L(SEt)(dmpe)]$ **2** and $[NEt_4]_2[MoFe_3S_4L(tccat)(solv)]$ (solv = dmso **4** or MeCN **5**) respectively. Cluster **2** reacted with 1 equivalent of trimethylacetyl chloride to give $[NEt_4][MoFe_3S_4L(Cl)(dmpe)]$ **3**. The clusters **2**–**5** have been characterised by ^1H NMR, IR and Mössbauer spectroscopies and by elemental microanalyses. Reaction of **4** with imidazole, tetraethylammonium imidazolate, or the tetraethylammonium salt of histidine methyl ester generated clusters, isolated as black solids, in which the molybdenum co-ordination environment, NO_2S_3, is similar to that of molybdenum in the iron–molybdenum cofactor of nitrogenase. Similar reactions were observed for the related cluster $[NEt_4]_2[MoFe_3S_4(SEt)_3(tccat)(solv)]$. Proton NMR, IR and Mössbauer parameters are reported.

Kim and Rees[1] have proposed, from an interpretation of the electron-density maps obtained from single-crystal X-ray studies on the iron–molybdenum protein of *Azotobacter vinelandii* and from previous spectroscopic data,[2] that the iron–molybdenum cofactor (FeMoco) of molybdenum nitrogenase has a stoichiometry Fe_7MoS_9(homocitrate) and the structure shown in Fig. 1 (homocitrate = 2-hydroxybutane-1,2,4-tricarboxylate). The molybdenum atom is co-ordinated by three sulfur, two oxygens from homocitrate and one nitrogen from histidine of the protein.

Over the past twenty years much effort has been put into the syntheses of chemical models for FeMoco.[2–4] Pertinent to this paper, Ciurli and Holm[5] have demonstrated the insertion of $\{MoFe_3S_4\}^{3+}$ and $\{VFe_3S_4\}^{2+}$ cores into a semi-rigid trithiolate cavitand ligand and discussed regiospecific reactions at the vanadium atom. There are also many examples of substitution at molybdenum in clusters containing the $\{MoFe_3S_4\}^{3+}$ core.[3,6] Coucouvanis *et al.*[7] have recently demonstrated that polycarboxylate anions can be co-ordinated to the molybdenum centre of $\{MoFe_3S_4\}^{3+}$ clusters, for example the cluster $[NEt_4]_3[MoFe_3S_4Cl_4(C_2O_4)]$ has been isolated and characterised by X-ray crystallography. Some of these clusters exhibit catalytic activity in the reduction of hydrazine to ammonia.[8] None of the reported clusters has molybdenum in a co-ordination environment identical to that of molybdenum in FeMoco.

We have previously shown that a range of amino acids, including histidine methyl ester, can bind to the $\{Fe_4S_4\}^{2+}$ core[9] and that cysteine ethyl ester and tyrosine methyl ester can bind to the cluster iron atoms in the bridged cubane $[Mo_2Fe_7S_8(SEt)_{12}]^{3-}$.[10] We have also shown that the tridentate thiolate proligand 1,4,7-tris(4-sulfanylbenzoyl)-1,4,7-triazacyclononane (H_3L) on deprotonation can bind three iron atoms of an $\{Fe_4S_4\}^{2+}$ cubane to give a 3:1 site-differentiated cluster.[11] Here we report binding of the $\{MoFe_3S_4\}^{3+}$ core by the ligand L and also the preparation of molybdenum–iron–sulfur clusters which contain molybdenum in a co-ordination environment, NO_2S_3, similar to that proposed for molybdenum in the FeMoco of molybdenum nitrogenase.

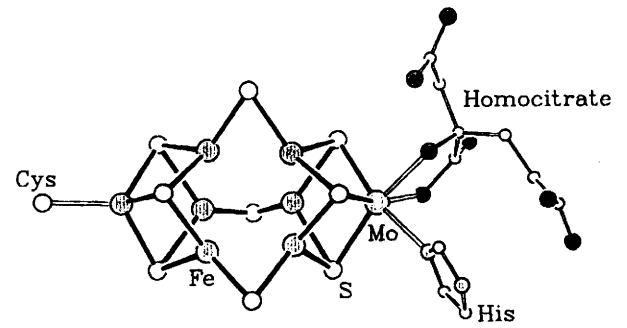
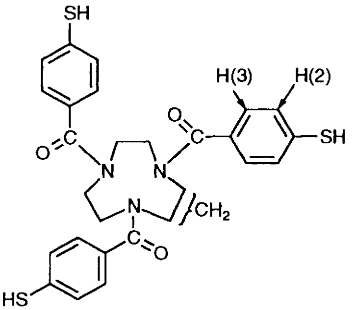


Fig. 1 Proposed structure of FeMoco from *Azotobacter vinelandii* nitrogenase molybdenum–iron protein[1]



H_3L

Results and Discussion

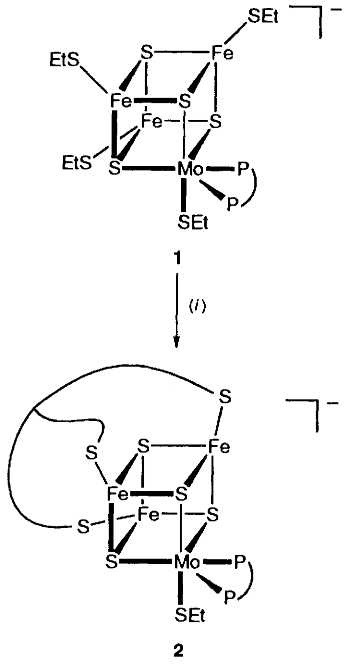
Ligation of $\{MoFe_3S_4\}^{3+}$ *by Trithiolate.*—The iron–sulfur cluster $[Fe_4S_4(SEt)_4]^{2-}$ has been shown[11] to react with the tridentate trithiol (H_3L) to form a 3:1 site-differentiated cluster, equation (1). Heterometallic iron–sulfur clusters,

$$[Fe_4S_4(SEt)_4]^{2-} + H_3L \longrightarrow [Fe_4S_4L(SEt)]^{2-} + 3HSEt \quad (1)$$

containing the $\{MoFe_3S_4\}^{3+}$ core, react with H_3L in a similar way to give clusters in which each of the iron atoms is co-ordinated by thiolate sulfur and in which the molybdenum is the differentiated site. Reaction of $[NEt_4][MoFe_3S_4(SEt)_4(dmpe)]$ **1** [dmpe = 1,2-bis(dimethylphosphino)ethane] with a stoichiometric amount of H_3L in dimethyl sulfoxide (dmso) gave $[NEt_4][MoFe_3S_4L(SEt)(dmpe)]$ **2** (Scheme 1). This cluster reacts with trimethylacetyl chloride to form a cluster with chloride substituted at the molybdenum only, equation (2).

$$[MoFe_3S_4L(SEt)(dmpe)]^- + Me_3CCOCl \longrightarrow [MoFe_3S_4L(Cl)(dmpe)]^- + Me_3CCOSEt \quad (2)$$

Related clusters, $[NEt_4]_2[MoFe_3S_4L(tccat)(solv)]$ (H_2tccat = 3,4,5,6-tetrachlorocatechol; solv = dmso **4** or MeCN **5**), were prepared from the reaction of the catechol-bridged dicubane $[NEt_4]_4[Mo_2Fe_6S_8(SEt)_6(tccat)_2]$, which in solution is cleaved to form the monocubane $[MoFe_3S_4(SEt)_3(tccat)(solv)]^{2-}$, with H_3L. The clusters **2**–**5** were isolated in good yield (65–75%) and were unambiguously characterised by ^{1}H NMR and Mössbauer spectroscopies and elemental microanalyses. Attempts to grow crystals of a quality suitable for X-ray crystallographic examination have, as yet, failed.



Scheme 1 P⌒P = dmpe. (*i*) H_3L

The ^{1}H NMR parameters for clusters **2**–**5** are collected in Table 1. The isotropically shifted signals, which arise due to the presence of the $\{MoFe_3S_4\}^{3+}$ core, with a $S = \frac{3}{2}$ ground state, were assigned by comparison to reported data for $[Fe_4S_4L(X)]^{2-}$ (ref. 11) and $[MoFe_3S_4(SEt)_4(dmpe)]^-$.[12] The resonances of the ligand (L) exhibit greater isotropic shifts than those for the ligand (L) in $[Fe_4S_4L(X)]^{2-}$ due to the greater paramagnetism of the heterometallic cluster core. The resonances assigned to H(3), exhibit the greatest isotropic shift. The upfield and downfield shifts relative to the diamagnetic shifts of H(2) (≈2.5 ppm) and H(3) (≈ −7 to −10 ppm) are consistent with a dominant contact-shift mechanism.[5]

For clusters **2** and **3** only one signal is observed for the dmpe-methyl and one for the dmpe-methylene protons. These resonances are slightly shifted downfield compared to those of the parent cluster **1**.[5] More signals may have been expected due to the possible various conformations of the Mo–dmpe ring, however such degenerate chemical shifts have been reported for related clusters.[12] On increasing the temperature the isotropically shifted signals of the dmpe protons move to higher field, Fig. 2, and the linewidths sharpen. The shifted ethanethiolate resonances of **2** move toward the diamagnetic shift on increasing temperature. An analogous effect, for both dmpe and ethanethiolate protons, was observed for cluster **1**.[12] The temperature dependence of the shifts of the ligand H(2) and CH_2 protons follows the established pattern,[11] moving downfield with increase in temperature. However, H(3) is anomalous in that the shift from the diamagnetic resonance decreases on raising the temperature. We have shown that

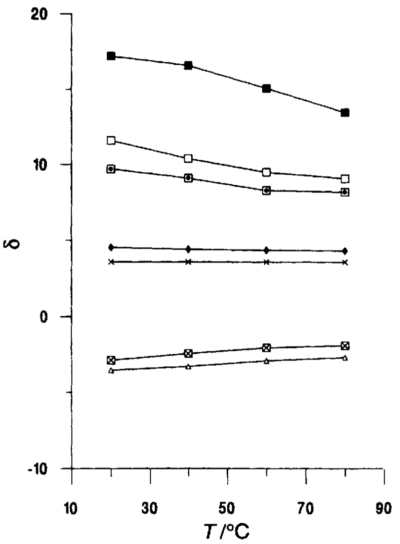


Fig. 2 Variation of ^{1}H NMR chemical shifts with temperature for $[NEt_4][MoFe_3S_4L(SEt)(dmpe)]$ **2** [≈2.5 × 10^{-3} mol dm^{-3} in $(CD_3)_2SO$]: (■) H(3), (□) CH_2 (of dmpe), (⊡) CH_3 (of dmpe), (◆) H(2), (×) CH_2, (⊠) CH_2 (of SEt) and (△) CH_3 (of SEt)

Table 1 Proton NMR parameters (δ) for tripodal thiolate-bound $\{MoFe_3S_4\}^{3+}$ clusters in $(CD_3)_2SO$ at ambient temperature[a]

	L					dmpe	
Cluster	H(3)	H(3′)	H(2)	H(2′)	CH_2	CH_2	CH_3
2 $[NEt_4][MoFe_3S_4L(SEt)(dmpe)]$[b]	17.2	—	4.53	—	3.60	11.6	9.70
3 $[NEt_4][MoFe_3S_4L(Cl)(dmpe)]$	14.0	—	4.86	—	3.65	11.3	9.10
4 $[NEt_4]_2[MoFe_3S_4L(tccat)(dmso)]$	14.7	13.3	4.50	4.35	3.82	—	—
5 $[NEt_4]_2[MoFe_3S_4L(tccat)(NCMe)]$[c]	17.0	15.8	6.06	4.67	3.82	—	—

[a] For all clusters, δ($[NEt_4]^+$) 3.20 (CH_2) and 1.25 (CH_3). [b] δ(SEt) −2.90 (CH_2) and −3.55 (CH_3). [c] In CD_3CN.

although room-temperature NMR spectra are consistent with a dominant contact mechanism, a more refined theory is required to explain the shifts and temperature dependencies in detail.[11] A similar dependence of isotropic shift on temperature was observed for clusters **4** and **5**, Fig. 3, signals for H(3) moving toward and H(2) moving away from the diamagnetic resonance on increasing temperature.

It has been reported[5] for clusters of the type $[MoFe_3S_4L'(tccat)(solv)]^{2-}$ [H_3L' = 1,3,5-tris(4,6-dimethyl-3-sulfanylphenylsulfanyl)-2,4,6-tris(*p*-tolylsulfanyl)benzene] that the ^1H NMR spectrum was indicative of trigonal symmetry, arising from fluxionality at the molybdenum site involving solvent dissociation, chelate-ring reorientation and solvent rebinding.[13] Only one signal was observed for each of the ligand protons. In clusters where solvent is replaced by a strongly binding ligand the fluxionality is not possible and the effective symmetry is reduced to C_{2v}. The ligand proton signals in such clusters were observed to be split into doublets. Surprisingly, in the clusters we describe above, the opposite situation is apparent. Clusters **2** and **3**, which have strongly binding SEt and Cl respectively, exhibit only one isotropically shifted signal for each of the ligand phenyl-ring protons. However, clusters **4** and **5**, in which solvent is co-ordinated to molybdenum, exhibit two signals for each of H(2) and H(3), Table 1. This implies that **2** and **3**, although the SEt and Cl are unlikely to dissociate in solution, exhibit time-averaged trigonal symmetry. Conversely in **4** and **5**, where it is expected that solvent exchange would facilitate catecholate-ring reorientation and, therefore, overall trigonal symmetry, there is differentiation between the two iron atoms off and one iron atom on the mirror plane which bisects the Mo–tccat ring. This is manifest by a difference between the chemical shift of the ligand phenyl protons associated with the sulfur bound to those irons off and on the mirror plane. The cause of this behaviour remains to be defined, although several alternative mechanisms have been proposed for related systems.[14]

The Mössbauer parameters for clusters **2**–**5** are listed in Table 2. Spectra were fitted by Lorenzian curves with no constraint placed on the intensity ratio. In each case the spectrum can be resolved into two quadrupole-split doublets of relative intensity 2 : 1, as predicted for two iron atoms off and one iron atom on the mirror plane bisecting the chelate ring (dmpe or tccat) at molybdenum. Representative spectra are illustrated by Figs. 4 and 5. The isomer shift (i.s.) and quadrupole splitting (q.s.) values are fully consistent with the formulations given and are similar to those observed for, for example, $[NEt_4]_2[MoFe_3S_4(SEt)_3(tccat)(dmso)]$, Table 2, and for $[NEt_4]_3[MoFe_3S_4(SC_6H_4Cl\text{-}4)_4(dacat)]$ (H_2dacat = 3,6-diallylcatechol; i.s. = 0.40 and 0.43; q.s. = 1.76 and 1.14 mm s^{-1}).[15] The lower i.s. compared to those for the chloro-substituted cluster $[NEt_4]_2[MoFe_3S_4Cl_3(tccat)(thf)]$ are as expected when chloride is replaced by alkane- or arene-thiolate.

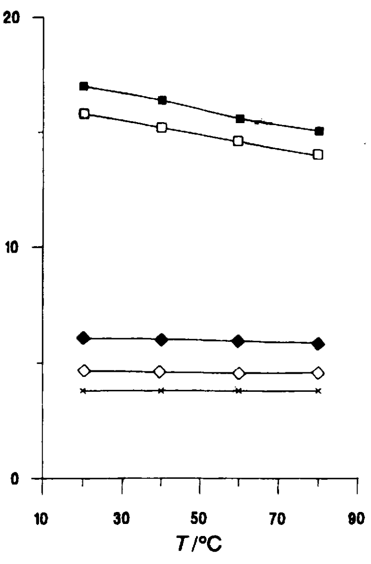


Fig. 3 Temperature dependence of ^1H NMR chemical shifts for $[NEt_4]_2[MoFe_3S_4L(tccat)(NCMe)]$ **5** (≈2.5 × 10^{-3} mol dm^{-3} in CD_3CN): (■) H(3), (□) H(3′), (◆) H(2), (◇) H(2′) and (×) CH_2

Binding of Imidazole and Histidine to Molybdenum in $\{MoFe_3S_4\}^{3+}$ *Clusters.*—In solution (dmso, MeCN) the dicubane $[NEt_4]_4[Mo_2Fe_6S_8(SEt)_6(tccat)_2]$ is cleaved to form the monocubane $[MoFe_3S_4(SEt)_3(tccat)(solv)]^{2-}$.[14] It has been shown that solvent in this and related clusters can be replaced by a wide range of ligands, including RS^-, CN^-, RO^-, PR_3, N_3^-, N_2H_4, NH_3, $PhNHNH_2$ and piperidine.[13,14,16] In some cases solids have been isolated and characterised and in others the products have been characterised in solution by ^1H NMR spectroscopy.

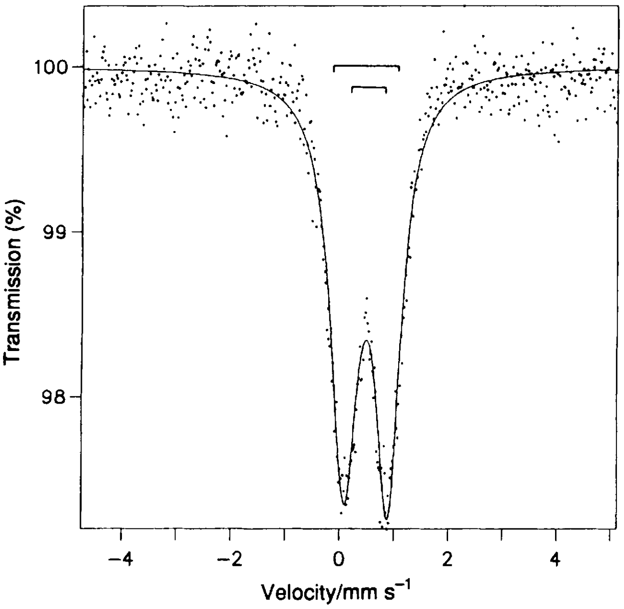


Fig. 4 Mössbauer spectrum of $[NEt_4][MoFe_3S_4L(SEt)(dmpe)]$ **2** at 77 K

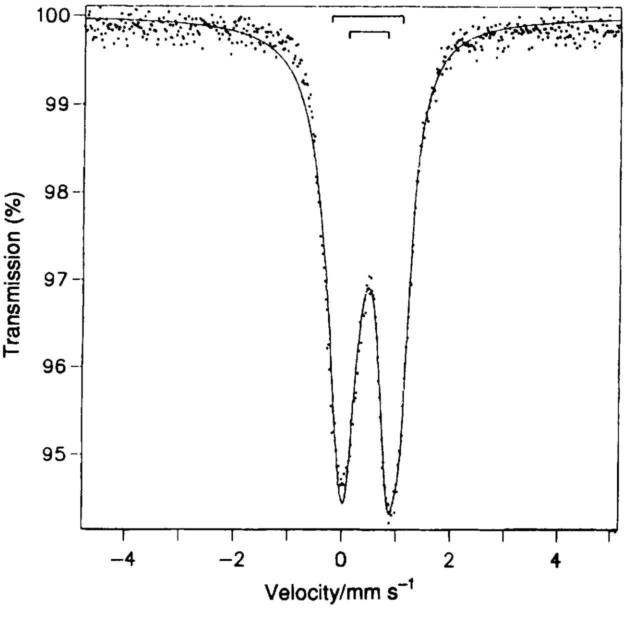


Fig. 5 Mössbauer spectrum of $[NEt_4]_2[MoFe_3S_4L(tccat)(dmso)]$ **4** at 77 K

Table 2 Mössbauer spectral parameters, solid state, zero field, 77 K relative to iron foil at 298 K

Complex[a]	i.s.	q.s.	h.w.h.m.[b]	Relative intensity
		mm s^{-1}		
$[Mo_2Fe_6S_8(SEt)_6(tccat)_2]^{4-}$	0.44(1)	1.43(2)	0.19(1)	1
	0.41(1)	0.97(1)	0.24(1)	2
$[MoFe_3S_4Cl_3(tccat)(thf)]^{2-}$	0.51(1)	1.33(2)	0.20(1)	1
	0.50(1)	0.86(2)	0.22(1)	2
$[MoFe_3S_4(SEt)_3(tccat)(dmso)]^{2-}$[c]	0.43(1)	1.38(6)	0.20(4)	1
	0.40(1)	0.91(5)	0.28(2)	2
2 $[MoFe_3S_4L(SEt)(dmpe)]^{-}$	0.46(1)	1.19(5)	0.21(3)	1
	0.48(1)	0.66(4)	0.25(2)	2
3 $[MoFe_3S_4L(Cl)(dmpe)]^{-}$	0.46(1)	1.20(3)	0.24(2)	1
	0.47(1)	0.68(2)	0.28(1)	2
4 $[MoFe_3S_4L(tccat)(dmso)]^{2-}$	0.44(1)	1.26(2)	0.23(1)	1
	0.47(1)	0.74(1)	0.26(2)	2
5 $[MoFe_3S_4L(tccat)(NCMe)]^{2-}$	0.43(1)	1.32(1)	0.20(1)	1
	0.42(1)	0.86(1)	0.22(1)	2
6 $[MoFe_3S_4L(tccat)(im)]^{3-}$	0.42(1)	1.33(5)	0.24(3)	1
	0.43(1)	0.71(4)	0.25(2)	2
8 $[MoFe_3S_4L(tccat)(HisOMe)]^{3-}$	0.44(1)	0.96(2)	0.33(1)	*d*
9 $[MoFe_3S_4(SEt)_3(tccat)(Him)]^{2-}$[c]	0.43(1)	1.39(6)	0.20(3)	1
	0.42(1)	0.91(1)	0.24(1)	2
10 $[MoFe_3S_4(SEt)_3(tccat)(im)]^{3-}$	0.42(1)	1.24(9)	0.24(4)	1
	0.41(1)	0.76(8)	0.23(3)	2
	[c]0.42(1)	1.09(1)	0.30(1)	*d*
11 $[MoFe_3S_4(SEt)_3(tccat)(HHisOMe)]^{2-}$[c]	0.46(2)	1.30(7)	0.22(2)	1
	0.40(1)	0.90(5)	0.26(2)	2

[a] Counter ion $[NEt_4]^+$ in all cases. [b] h.w.h.m. = Half-width at half-maximum. [c] Frozen dmso solution. [d] Unable to resolve overlapping doublets.

Substitution at molybdenum in $[NEt_4][MoFe_3S_4(SEt)_4(dmpe)]$ has been explored little. Reaction with 5 equivalents of benzoyl chloride in MeCN gave chloride substitution at both the iron and molybdenum,[12] equation (3).

$$[MoFe_3S_4(SEt)_4(dmpe)]^- + 4PhCOCl \longrightarrow [MoFe_3S_4Cl_4(dmpe)]^- + 4PhCOSEt \quad (3)$$

No substitutions at molybdenum in $[MoFe_3S_4L'(tccat)(solv)]^{2-}$ have been reported.[5]

Reaction of the trithiolate-ligated cluster **4** with tetraethylammonium imidazolate ($[NEt_4][im]$), imidazole (Him), and $[NEt_4][HisOMe]$(HHisOMe = histidine methyl ester) in dmso gave novel clusters $[NEt_4]_3[MoFe_3S_4L(tccat)(im)]$ **6**, $[NEt_4]_2[MoFe_3S_4L(tccat)(Him)]$ **7** and $[NEt_4]_3[MoFe_3S_4L(tccat)(HisOMe)]$ **8**, respectively. The black solids exhibited an IR carbonyl stretch at 1630 cm^{-1} from the trithiolate ligand carbonyl and for **8** an additional carbonyl stretch at 1737 cm^{-1} from the histidine ester carboxylate. This compares to a carbonyl stretch of 1724 cm^{-1} for unco-ordinated histidine methyl ester. Similarly reaction of $[NEt_4]_4[Mo_2Fe_6S_8(SEt)_6(tccat)_2]$ with Him, $[NEt_4][im]$ and HHisOMe in MeCN gave $[NEt_4]_2[MoFe_3S_4(SEt)_3(tccat)(Him)]$ **9**, $[NEt_4]_3[MoFe_3S_4(SEt)_3(tccat)(im)]$ **10** and $[NEt_4]_2[MoFe_3S_4(SEt)_3(tccat)(HHisOMe)]$ **11**. Clusters **9** and **11** were obtained as black gums and **10** as a black solid. The histidine ester carboxylate IR stretch of **11** was observed at 1740 cm^{-1}. In no case, as yet, has it been possible to grow crystals suitable for X-ray crystallography. However, the identity of the materials and their full or substantial purity were established by ^1H NMR and Mössbauer spectroscopies.

The ^1H NMR parameters for clusters **6**–**11** are collected in Table 3. For **6**–**8** the ligand (L) H(3) protons have chemical shifts similar to those of the solvated cluster **4**; ligand (L) H(2) protons are shifted *ca.* 3.5 ppm downfield relative to those in **4**. The H(2) protons, being closest to the $\{MoFe_3S_4\}^{3+}$ core, are the most sensitive to substitution at the molybdenum. Both for H(2) and H(3) only one signal was observed. The NMR of ethanethiolate-ligated clusters **10** and **11** show a differentiation of the ethanethiolate ligand bound to iron on and irons off the mirror plane which bisects the Mo–tccat ring. The thiolate methylene signals are separated by *ca.* 30 ppm compared to a separation of 41 ppm found for the signals of the cluster $[MoFe_3S_4(SEt)_3(tccat)(CN)]^{3-}$ (SCH_2, δ 79 and SCH'_2, 38).[14] The molybdenum imidazolate cluster **10** shows the largest separation of the thiolate methylene signals of 56 ppm (see below). The thiolate methyl resonances are also split and appear at δ *ca.* 5.5–6.0 and 4, a much smaller shift from the diamagnetic position than for the corresponding methylene signals. No signals are observed from the parent cluster $[NEt_4]_4[Mo_2Fe_6S_8(SEt)_6(tccat)_2]$ in solution (SCH_2CH_3, δ 53.2; SCH_2CH_3, 4.32).

Imidazole ring protons in clusters **6**, **7**, **9** and **10** appear at approximately δ 9.2 and 12.3, shifted upfield only slightly (≈ 1 and 5 ppm) when compared to the diamagnetic resonance. Histidine ring protons of **8** and **11** shift upfield by a similar extent. Others have noted[16] that ligands bound to molybdenum exhibit isotropic shifts much less than those bound at the iron atoms of a molybdenum–iron–sulfur cluster. The α-CH and β-CH_2 protons of co-ordinated histidine are unobserved in the range δ −20 to 120. The absence of the signals may be attributed to line broadening or to concealment under more intense signals. In no case was there any evidence of substitution of imidazole or histidine at the cluster iron atoms.

Ligand (L) proton signals in clusters **6**–**8** show a temperature dependence similar to that of the parent cluster **4**. The H(2) protons move away from and the H(3) protons toward the diamagnetic resonance on increasing the temperature. The isotropically shifted NMR signals for the Mo–im cluster **6** are shown in Fig. 6.

Ethanethiolate SCH_2CH_3 and SCH_2CH_3 isotropically shifted signals for clusters **9**–**11** all move back toward the diamagnetic on increasing temperature, as observed for the parent cluster $[MoFe_3S_4(SEt)_3(tccat)(dmso)]^{2-}$ in $(CD_3)_2SO$ solution, Fig. 7. No coalescence of SCH_2 signals was observed on increasing temperature, showing that stereochemical rigidity of the cluster was maintained. Imidazole- and histidine-ring protons also move toward the diamagnetic on increasing

Table 3 Proton NMR parameters (δ) for $\{MoFe_3S_4\}^{3+}$ clusters with imidazole or histidine methyl ester bound at molybdenum. Ambient temperature in $(CD_3)_2SO$[a]

	L			Imidazole		Histidine[b]			Ethanethiolate			
Cluster	H(3)	H(2)	CH_2	H	H	H	H	CO_2Me	CH_2	CH'_2	CH_3	CH'_3
6	17.0	8.10	3.60	12.2	9.45	—	—	—	—	—	—	—
7	17.0	8.10	3.60	12.2	9.45	—	—	—	—	—	—	—
8	13.4	7.92	3.60	—	—	11.9	9.4	3.9	—	—	—	—
9	—	—	—	12.1	8.70	—	—	—	72	43	5.30	*c*
10	—	—	—	12.5	9.03	—	—	—	88	32	6.1	3.8
11	—	—	—	—	—	11.8	7.9	3.6	74	43	5.5	4.0

[a] $[NEt_4]^+$ cation signals at δ 3.20 and 1.25. [b] Histidine α-CH and β-CH_2 are not observed and are probably concealed. [c] Concealed.

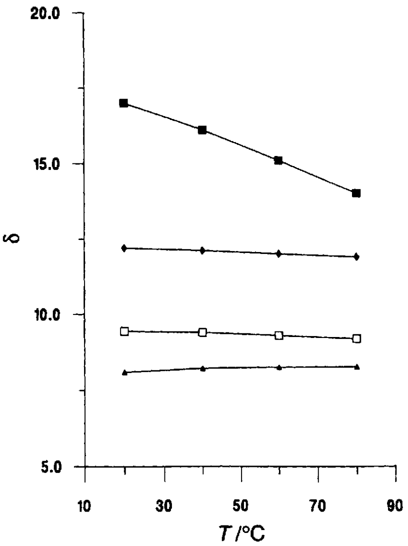


Fig. 6 Variation of ^1H NMR chemical shifts with temperature for $[NEt_4]_3[MoFe_3S_4L(tccat)(im)]$ **6** [≈2.5 × 10^{-3} mol dm^{-3} in $(CD_3)_2SO$]: (■) H(3), (◆) H of im, (□) H of im and (▲) H(2)

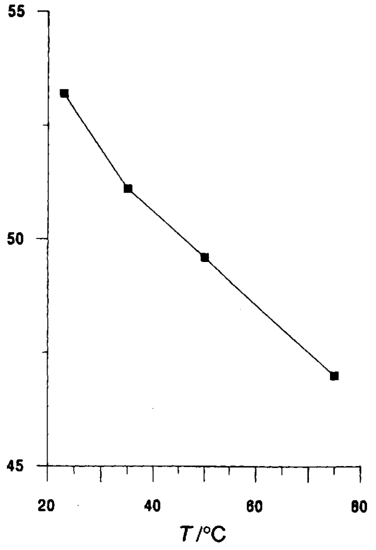


Fig. 7 Temperature dependence of the ^1H NMR chemical shift of ethanethiolate methylene for $(CD_3)_2SO$-cleaved $[Mo_2Fe_6S_8(SEt)_6(tccat)_2]^{4-}$

temperature. Together, the above NMR observations unequivocally demonstrate that substitution has occurred at the molybdenum and, at least for the ethanethiolate-ligated clusters, that the clusters are stereochemically rigid.

To establish the mode of binding of imidazole and of histidine to the molybdenum of the cluster a series of *in situ* ^1H NMR experiments was performed. The sensitivity of the isotropically shifted ethanethiolate methylene signal to coordination at molybdenum was used as a probe. The cluster $[NEt_4]_4[Mo_2Fe_6S_8(SEt)_6(tccat)_2]$ in both CD_3CN and $(CD_3)_2SO$ solutions was treated with Him, 1-methylimidazole (mim) and $[NEt_4][im]$ and, in $(CD_3)_2SO$ only, with HHisOMe. The thiolate methylene chemical shifts observed are given in Table 4. Him Imidazole has a considerable partial negative charge on N(3) and a fractional positive charge on N(1) and is expected to bind to molybdenum through N(3). 1-Methylimidazole cannot deprotonate at N(1) so under no circumstances is able to bind as an imidazolate anion. It can only bind to molybdenum through the lone pair of electrons on N(3); the lone pair on N(1) is part of the aromatic π-electron system. The SCH_2 chemical shifts for products of the reaction of mim are, within experimental limits, the same as those for products from the reaction of Him in CD_3CN and for Him and HHisOMe in $(CD_3)_2SO$. By implication mim, Him and HHisOMe all bind through N(3) as neutral ligands. On reaction of solutions of the cluster with $[NEt_4][im]$ different thiolate methylene chemical shifts were observed, the separation between the two methylene signals increasing from 14 to 45 (CD_3CN) and from 25–30 to 56 ppm [$(CD_3)_2SO$]. In this case we propose that binding is through the anionic imidazolate N(1) and by analogy, when $[NEt_4][HisOMe]$ is employed as reagent, it would bind as an anion. The NMR resonances of the imidazole- and histidine-ring protons are insensitive to the mode of binding, Table 3.

Table 2 lists the Mössbauer parameters for clusters **6** and **8**–**11**. In all but two cases the spectrum can be resolved into two quadrupole-split doublets of relative intensity 1:2 (no constraints on fitting), as was expected (see above). Clusters **8** and **10** exhibit broadened spectra which cannot be resolved; the larger linewidth is, however, indicative of inequivalence of iron sites. The i.s. and q.s. values of all of the clusters are similar to those of the parent solvated clusters described above and fully consistent with the formulations given. The i.s. are not affected by the mode of binding of, for example, the imidazole. In **9**, Fig. 8, where binding is through N(3) and the imidazole can be described as a neutral ligand, i.s. of 0.43(1) and 0.42(1) mm s^{-1} are observed. Similarly in **10**, where binding is through N(1) and the ligand can be described as imidazolate, i.s. of 0.42(1) and 0.41(1) mm s^{-1} are observed. This reflects that, although the overall charge of the cluster–ligand complex has changed, the $\{MoFe_3S_4\}^{3+}$ core charge and, therefore, the mean oxidation state of each iron atom has not changed.

Conclusion

Four novel clusters, **2**–**5**, in which the iron atoms of the $\{MoFe_3S_4\}^{3+}$ core are ligated by a tridentate thiolate, have been prepared and characterised. Reaction of **4** with Him, $[NEt_4][im]$ or $[NEt_4][HisOMe]$ generates new materials **6**–**8**, in which imidazole/histidine binds at molybdenum. Similar

Table 4 Proton NMR chemical shifts (δ) for ethanethiolate CH_2 of the products generated *in situ* from the reaction of $[MoFe_3S_4(SEt)_3(tccat)(solv)]^{2-}$ [solv = CD_3CN or $(CD_3)_2SO$] with imidazole, 1-methylimidazole, tetraethylammonium imidazolate and histidine methyl ester

	CD_3CN		$(CD_3)_2SO$	
Reagent	CH_2	CH'_2	CH_2	CH'_2
Him	64	50	72	43
mim	64	49	69	44
$[NEt_4][im]$	82	37	88	32
HHisOMe	—	—	74	43

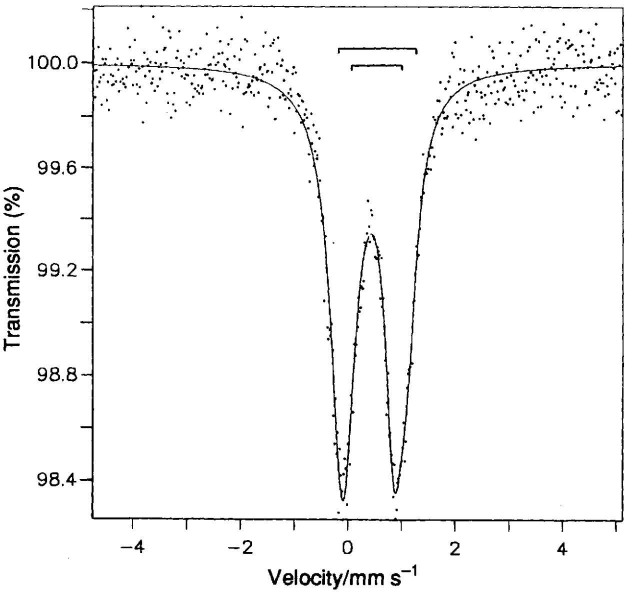


Fig. 8 Mössbauer spectrum of $[NEt_4]_2[MoFe_3S_4(SEt)_3(tccat)(Him)]$ **9** in frozen dmso solution at 77 K

products, **9**–**11**, are obtained on reaction of the heterometallic cluster $[MoFe_3S_4(SEt)_3(tccat)(dmso)]^{2-}$, where the iron atoms are ligated by ethanethiolate, with Him, $[NEt_4][im]$ and HHisOMe. Only when the tetraethylammonium salt of imidazole or histidine is employed as reagent is binding to molybdenum through anionic N(1); in all other cases binding is, as a neutral molecule, through N(3). The cluster complexes **6**–**11** all contain molybdenum in a co-ordination environment, NO_2S_3, similar to that found for molybdenum in FeMoco of molybdenum nitrogenase.

Demadis and Coucouvanis[18] have recently reported the crystal structure of an $\{MoFe_3S_4\}^{3+}$ cluster in which molybdenum is ligated by methyliminodiacetate. The molybdenum is co-ordinated by two carboxylates and an imino nitrogen atom. The environment about molybdenum is similar to that found in FeMoco.

Experimental

General Methods and Physical Techniques.—All solvents were distilled from appropriate drying agents and degassed before use. Standard syringe and Schlenk techniques were employed when handling air-sensitive materials.

1,4,7-Tris(4-sulfanylbenzoyl)-1,4,7-triazacyclononane (H_3L) was prepared by the published procedure.[11] The metal–sulfur clusters $[NEt_4][MoFe_3S_4(SEt)_4(dmpe)]$ **1**, $[NEt_4]_4[Mo_2Fe_6S_8(SEt)_6(tccat)_2]$ and, with a minor adaptation (using trimethylacetyl chloride), $[NEt_4]_2[MoFe_3S_4Cl_3(tccat)(thf)]$ (thf = tetrahydrofuran) were prepared by standard procedures.[12–14] Histidine methyl ester dihydrochloride was obtained from Aldrich Chemical and treated with 2 equivalents of potassium *tert*-butoxide in methanol to give histidine methyl ester. All other chemicals were from Aldrich Chemical and used as supplied.

Infrared spectra were recorded as KBr discs, on a Perkin-Elmer 883 or 16F PC FT-IR spectrometer. Mössbauer parameters were determined at 77 K on an ES-technology MS105 spectrometer using a 925 MBq ^{57}Co source in a rhodium matrix at ambient temperature, and were referenced against a 25 μm iron foil at 298 K. Frozen-solution Mössbauer samples were prepared and mounted as previously described.[17] Proton NMR spectra were obtained on a JEOL GSX 270 or Varian Unity 300 spectrometer and were referenced against $SiMe_4$. Microanalyses were performed by Dr. R. Ortiz (University of Murcia) using a Carlo Erba EA-1108 analyser.

Syntheses.—$[NEt_4][MoFe_3S_4L(SEt)(dmpe)]$ **2**. The compound H_3L (0.093 g, 0.173 mmol) dissolved in dmso (2 cm^3) was added to a solution of $[NEt_4][MoFe_3S_4(SEt)_4(dmpe)]$ **1** (0.159 g, 0.173 mmol). After stirring the mixture under reduced pressure, at 313 K, for 1 h, diethyl ether (40 cm^3) was added to precipitate the product as a black solid. This solid was washed with diethyl ether and dried *in vacuo* (0.165 g, 75%) (Found: C, 39.2; H, 5.3; N, 4.3; S, 20.3. $C_{43}H_{65}Fe_3MoN_4O_3P_2S_8$ requires C, 40.7; H, 5.2; N, 4.4; S, 20.2%), ν_{max} 1630 cm^{-1} (CO) (KBr).

$[NEt_4][MoFe_3S_4L(Cl)(dmpe)]$ **3**. To a solution of cluster **4** (0.072 g, 0.057 mmol) in dmso (5 cm^3) was added trimethylacetyl chloride (6.9 μl, 0.007 g, 0.058 mmol). The mixture was stirred for 1 h at 313 K, under reduced pressure. After cooling to room temperature, diethyl ether (40 cm^3) was added and the product precipitated as a black solid, which was washed with diethyl ether and dried *in vacuo* (0.046 g, 65%) (Found: C, 39.7; H, 5.2; N, 4.5; S, 18.3. $C_{41}H_{60}ClFe_3MoN_4O_3P_2S_7$ requires C, 39.6; H, 4.9; N, 4.5; S, 18.1%), ν_{max} 1630 cm^{-1} (CO) (KBr).

$[NEt_4]_2[MoFe_3S_4L(tccat)(dmso)]$ **4**. The cluster $[NEt_4]_4[Mo_2Fe_6S_8(SEt)_6(tccat)_2]$ **2** (0.023 g, 0.011 mmol) in dmso (5 cm^3) was added to H_3L (0.012 g, 0.022 mmol) in dmso (2 cm^3). The mixture was stirred under reduced pressure at 313 K for 1 h. Diethyl ether (40 cm^3) was then added, the black precipitate which formed was filtered off, washed with diethyl ether and dried *in vacuo* (0.021 g, 70%) (Found: C, 40.9; H, 6.3; N, 4.2; S, 14.6. $C_{51}H_{70}Cl_4Fe_3MoN_5O_6S_8$ requires C, 40.5; H, 4.7; N, 4.6; S, 16.9%), ν_{max} 1630 cm^{-1} (CO) (KBr).

$[NEt_4]_2[MoFe_3S_4L(tccat)(NCMe)]$ **5**. This cluster was prepared by the method above, except that acetonitrile was used as solvent (0.022 g, 68%) (Found: C, 40.1; H, 5.5; N, 4.9; S, 13.5. $C_{51}H_{67}Cl_4Fe_3MoN_6O_5S_7$ requires C, 41.6; H, 4.6; N, 5.7; S, 15.2%), ν_{max} 1630 cm^{-1} (CO) (KBr).

Substitutions at molybdenum. $[NEt_4][im]$. Sodium (0.23 g, 0.01 mol) dissolved in MeOH (50 cm^3) was treated with imidazole (0.68 g, 0.01 mol). Tetraethylammonium bromide (2.28 g, 0.01 mol) was added and the resultant solution stirred for 2 h. Solvent was removed *in vacuo* and the residue redissolved in acetonitrile (50 cm^3) and stirred for 1 h. A white precipitate of sodium bromide was filtered off, diethyl ether (20 cm^3) was added to the filtrate, and the mixture stored overnight at room temperature. The product was collected as a white crystalline solid in quantitative yield. $\delta_H[(CD_3)_2SO]$ 6.99 (H of im), 6.60 (H of im), 3.16 (NEt_4) and 1.18 (NEt_4).

$[NEt_4]_3[MoFe_3S_4L(tccat)(im)]$ **6**. A solution of cluster **4** (0.054 g, 0.036 mmol) in dmso (2 cm^3) was mixed with $[NEt_4][im]$ (0.005 g, 0.036 mmol) under reduced pressure for 1 h. Addition of diethyl ether (30 cm^3) precipitated a black solid, which was collected, washed with diethyl ether and dried *in vacuo* (0.042 g, 63%). ν_{max} 1630 cm^{-1} (CO) (KBr).

$[NEt_4]_2[MoFe_3S_4L(tccat)(Him)]$ **7**. Reaction of compound **4** (0.054 g, 0.036 mmol) with Him (0.0025 g, 0.036 mmol) in dmso (2 cm^3) for 3 h, followed by addition of diethyl ether (30 cm^3), gave a black solid with a ^1H NMR spectrum identical to that obtained for **6**.

$[NEt_4]_3[MoFe_3S_4L(tccat)(HisOMe)]$ **8**. A solution of cluster **4** (0.063 g, 0.042 mmol) in dmso (3 cm^3) was added to the tetraethylammonium salt of histidine methyl ester, $[NEt_4][HisOMe]$ (obtained from the reaction of histidine methyl ester dihydrochloride, 2 equivalents of potassium *tert*-butoxide and 1 equivalent of tetraethylammonium hydroxide in MeOH) (0.012 g, 0.042 mmol) in dmso (2 cm^3). After stirring for 2 h diethyl ether (30 cm^3) was added to precipitate the product as a black solid which was collected, washed with diethyl ether and dried *in vacuo* (0.056 g, 74%). ν_{max} 1630, 1737 cm^{-1} (CO) (KBr).

$[NEt_4]_2[MoFe_3S_4(SEt)_3(tccat)(Him)]$ **9**. To a stirred solution of $[NEt_4]_4[Mo_2Fe_6S_8(SEt)_6(tccat)_2]$ (0.64 g, 0.29 mmol) in MeCN (30 cm^3) was added a solution of imidazole (Him) (0.05 g, 0.73 mmol) in MeCN (10 cm^3). After stirring for 2 h solvent was removed to give the product as a black gum.

$[NEt_4]_3[MoFe_3S_4(SEt)_3(tccat)(im)]$ **10**. This cluster was prepared by a similar procedure to **9**, but using $[NEt_4][im]$ in MeCN, as a black solid.

$[NEt_4]_2[MoFe_3S_4(SEt)_3(tccat)(HHisOMe)]$ **11**. The cluster $[NEt_4]_4[Mo_2Fe_6S_8(SEt)_6(tccat)_2]$ (0.25 g, 0.12 mmol) and histidine methyl ester (0.049 g, 0.29 mmol) were stirred together in MeCN (30 cm^3) for 2 h. On taking to dryness the product was obtained as a black gum. ν_{max} 1740 cm^{-1} (CO) (KBr).

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